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TASK I

Establishment of the Feasibility of a Process Capable of Low Cost, High Volume Production of Silane, SiH_4

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QUARTERLY PROGRESS REPORT

BY
W.C. BRENEMAN
J.Y.P. MUI

October 15, 1976

Period Covered: July 1976 - October 1976

JPL CONTRACT 954334

UNION CARBIDE CORPORATION
CHEMICALS AND PLASTICS
SISTERSVILLE, WEST VIRGINIA

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology under NASA Contract NAS 7-100 for the U.S. Energy Research and Development Administration, Division of Solar Energy.

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TASK I

Establishment of The Feasibility of A
Process Capable of Low Cost,
High Volume Production of Silane, SiH_4

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The JPL Low Cost Silicon Solar Array Project is funded by ERDA and forms part of the ERDA Photovoltaic Conversion Program to initiate a major effort toward the development of low cost solar arrays.

LOW COST SILICON SOLAR ARRAY PROJECT

TASK I

Establishment of The Feasibility of A Process Capable of Low Cost, High Volume Production of Silane, SiH_4

UNION CARBIDE CORPORATION
SISTERSVILLE, WEST VIRGINIA

W. C. BRENEMAN
J. Y. P. MUI

ABSTRACT

The study of a process for the low cost production of silane included laboratory investigations of the kinetics of the redistribution of dichlorosilane and trichlorosilane vapor over a tertiary amine ion exchange resin catalyst. The hydrogenation of $SiCl_4$ to form $HSiCl_3$ and the direct synthesis of H_2SiCl_2 from HCl gas an metallurigical silicon metal were also studied. The purification of SiH_4 using activated carbon adsorbent was studied along with a process for storing SiH_4 adsorbed on carbon. The latter makes possible a higher volumetric efficiency than the current practice of compressed gas storage.

The mini-plant designed to produce ten pounds per day of SiH_4 is nearly complete, a detailed description of the unit and its essential design features is given.

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INTRODUCTION

This research program commenced October 6, 1975. Its purpose is to determine the feasibility for the high volume, low cost production of silane (SiH_4) as an intermediate raw material for solar grade silicon metal. The process to be investigated is based on the synthesis of SiH_4 by the catalytic redistribution of chlorosilanes. The goal is to demonstrate the feasibility for a large scale production cost of under $5.00 per kilogram of SiH_4.

Prior to this program Union Carbide has shown experimentally that pure chlorosilanes can be redistributed into an equilibrium mixture of other hydrochlorosilanes by contact with a tertiary amine ion exchange resin. Patent rights for this process and improvements there on have been filed.

In the previous Quarterly Report, the equilibrium composition and kinetics of the vapor phase redistribution of dichlorosilane catalyzed by a macroreticular tertiary amine functional ion exchange resin were determined over a temperature range of 50 to 80°C. At 80°C, for example, the effluent vapor contained 14 mole percent SiH_4 at equilibrium while the time to reach 50% of that value was 0.25 seconds. Also studied was the hydrogenation of silicon tetrachloride to trichlorosilane. The results of that study indicated steady state levels of 15 to 22% trichlorosilane. Thus, with a means to convert silicon tetrachloride to trichlorosilane coupled to a redistribution sequence, a closed loop manufacturing sequence is possible to produce SiH_4 from hydrogen and silicon metal to wit:

$$2\ H_2 + Si + 3\ SiCl_4 \xrightarrow[Cu]{550°C} 4\ HSiCl_3$$

$$4\ HSiCl_3 \xrightarrow{\text{Redistribution}} 2\ H_2SiCl_2 + 2\ SiCl_4$$

$$2\ H_2SiCl_2 \xrightarrow{\text{Redistribution}} SiCl_4 + SiH_4$$

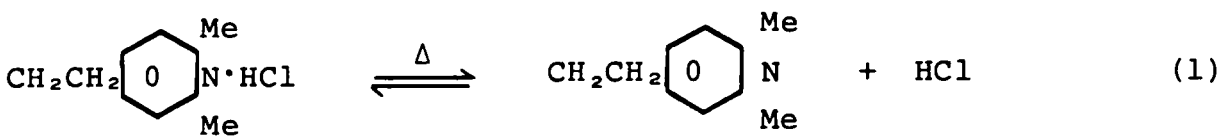
The design of a pilot scale plant for the production silane from dichlorosilane was completed and installation initiated This unit features internal recycle of by-product H_3SiCl and unreacted H_2SiCl_2, an on-line chromatograph sampling system and a purification section for removing traces of chlorosilanes from the product SiH_4 while not requiring ultra-low temperature refrigeration.

DISCUSSION

I. Laboratory Investigations

A. Disproportionation of H_2SiCl_2 to SiH_4

In checking out the yield of SiH_4 obtained by the disproportionation of H_2SiCl_2 over the same 10 g A-21 resin catalyst used in previous experiments,[1] a drop in the SiH_4 production rate was noted. This prompted a study on the catalytic activity of the A-21 resin over long periods of disproportionation reactions. The disproportionation of H_2SiCl_2 was repeated under the same experimental conditions with the same 10 g A-21 resin bed as reported in previous experiments. Results were summarized in Table I. Experiments 1, 2, 4, 5, 7 and 8 in Table I summarized the SiH_4 production rates and product compositions before and after about three months of operations. At low H_2SiCl_2 feedrate, 250 cc/minute, run number 1 and 2 showed little or no differences in SiH_4 production rate and SiH_4 yield in the product mixture. However, at higher H_2SiCl_2 feedrate, 500 cc/minute and 1000 cc/minute, a significant drop in SiH_4 production rate and SiH_4 yield was noted in run number 4, 5, and 7, 8. It was generally believed that the amine hydrochloride was the true catalyst for the disproportionation of hydrochlorosilanes. In the case of A-21 resin, the dimethylamine hydrochloride was bonded to a polystyrene resin support through a phenylethyl linkage. Amine hydrochlorides were known to dissociate at elevated temperature to free amine and HCl, viz., equation (1)



(1)

HCl might be gradually eluded from the A-21 resin bed. Since the free amine was known to be a poor catalyst for the disproportionation reaction, the lowering of the A-21 resin catalytic activity could be attributed to the loss of HCl. To test this hypothesis, the 10 g A-21 resin was treated with a 50:50 mixture of HCl and nitrogen at a constant flowrate of 500 cc/minute for a total of 10 minutes. Then, the same disproportionation reaction of H_2SiCl_2 was repeated under the same experimental conditions with the HCl-treated A-21 resin. Results of these experiments were given in run number 3, 6 and 9 in Table I. Data in Table I showed that the catalytic activity of the HCl-treated A-21 resin had indeed increased substantially. Both the SiH_4 production rate and SiH_4 yield in the product mixture were increased, compare run number 5, 6, and 8, 9 in Table I. However, in comparison with the rate data obtained three months ago, the HCl-treated A-21 resin still showed a lower catalytic activity; especially at high H_2SiCl_2 feed. For example, at 1000 cc/minute of H_2SiCl_2 feed, the HCl-treated A-21 resin showed a definite drop of catalytic activity from what it was three months ago, viz., run number 7 and 9 in Table I. One plausible explanation was that, in addition to chemically bonded amine, the A-21 resin also contained some free amine which was physically adsorbed onto the polystyrene resin support. This volatile amine and its amine hydrochloride might be slowly eluded from the A-21 resin bed after prolong operations. As a result, the reduced catalytic activity of the A-21 resin could be explained. The lowering of the A-21 resin catalytic activity due to the loss of HCl as illustrated in equation (1) could be readily restored by simply adding HCl gas to the resin bed. However, the lowering of the A-21 resin catalytic activity due to the loss of free amine hydrochloride could not be as conveniently restored. Nevertheless, even with this somewhat reduced A-21 resin catalytic activity, the rate of the disproportionation of H_2SiCl_2 to SiH_4 was still very high. A detailed study on the mechanism of the disproportionation reaction is planned.

TABLE I

TREATMENT OF A-21 RESIN WITH HCl GAS

Run Number	Date	Reaction Temperature °C	H_2SiCl_2 Feedrate cc/Minute	SiH_4 Production Rate cc/Minute	Production Composition, Mole %				
					SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
1	3-9-76	80	250	35.8	14.1	35.4	35.4	42.1	0.7
2	6-12-76	80	250	32.0	14.8	10.6	34.6	39.8	0.2
(A-21 treated with 250 cc/minute of HCl gas for 10 minutes.)									
3	6-13-76	80	250	36.8	14.9	10.6	34.3	40.1	0.2
4	3-9-76	80	500	64.6	12.9	10.0	33.6	42.9	0.5
5	6-12-76	80	500	47.0	10.8	12.6	41.7	34.8	0.08
(After HCl treatment.)									
6	6-13-76	80	500	60.5	12.6	11.9	38.1	37.3	0.09
7	3-9-76	80	1000	125	13.2	9.0	35.5	41.9	0.4
8	6-12-76	80	1000	58.3	7.3	14.1	49.8	28.8	0.03
(After HCl treatment.)									
9	6-13-76	80	1000	72.6	8.7	13.2	47.4	30.7	0.03

B. Disproporation of $HSiCl_3$ to H_2SiCl_2

The initial phase of the "mini" plant at Sistersville, West Virginia to manufacture SiH_4 will be using dichlorosilane as raw material. The final phase of the "maxi" plant will use trichlorosilane as the source of SiH . Although the liquid phase disproportionation of $HSiCl_3$ to make H_2SiCl_2 was well-known, the vapor phase disproportionation of $HSiCl_3$ might have some merits. Furthermore, comparison of the rate of disproportionation of H_2SiCl_2 with that of $HSiCl_3$ could provide useful information on the mechanism of the disproportionation reactions.

The disproportionation of $HSiCl_3$ was carried out at 60° in the same apparatus as described in previous experiments. The disproportionation of H_2SiCl_2 was first carried out to provide a reference standard on the reactivity of the 10 g A-21 resin catalyst. Then, trichlorosilane vapor was fed into the same resin bed and the rate of reaction was measured.

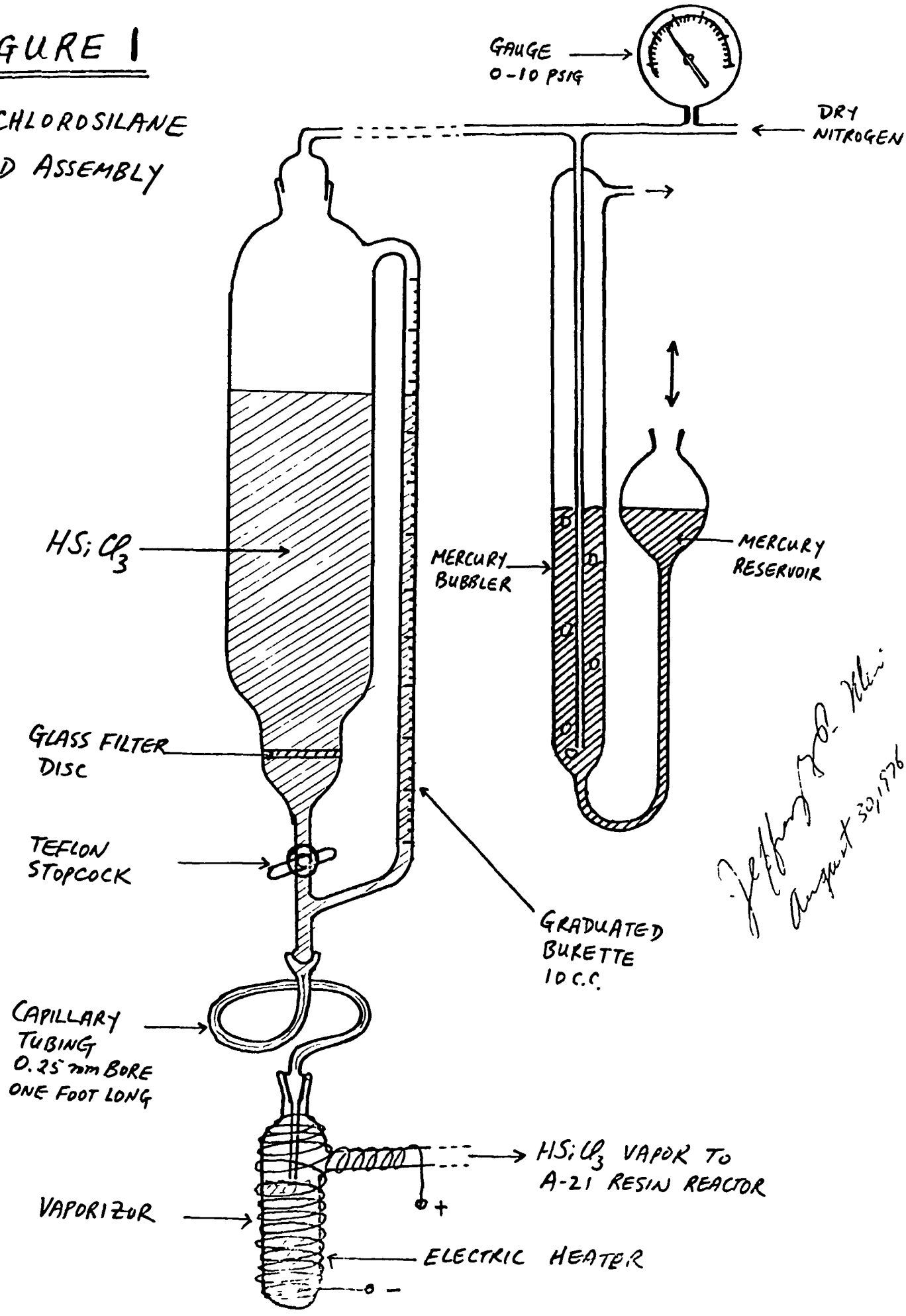
A method of feeding an accurate, constant flow of liquid into a reactor was described in Figure 1. Trichlorosilane (bp 31.9°) was placed in a dropping funnel equipped with a burette side arm, a filter disc and a Teflon stopcock. The flow of $HSiCl_3$ liquid was controlled by a capilliary tubing, which was described mathematically by the Law of Poiseuille,

$$V = \frac{\pi \, p \, \gamma^4}{8 \, l \, n} t$$

where V = volume of liquid escaped in time t
p = pressure difference between two ends of the tube
γ = radius
l = length
n = viscosity of the liquid

FIGURE 1

TRICHLOROSILANE FEED ASSEMBLY



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Since V, l, n remained constant, the flowrate, V/t, of $HSiCl_3$ was directly proportional to pressure p. Thus, a constant flowrate of $HSiCl_3$ could be readily achieved by maintaining a constant pressure head over the liquid. A convenient method to create a constant pressure of nitrogen gas was obtained by bubbling dry nitrogen into a column of mercury as shown in Figure 1. The flowrate of $HSiCl_3$ could be changed and adjusted by varying the nitrogen pressure from 0 to 10 psig by moving the mercury reservoir upward or downward. The flowrate of $HSiCl_3$ was measured and checked by closing the Teflon stopcock. The time required for the liquid level in the burette side arm to travel one unit volume between two markings was recorded and the $HSiCl_3$ flowrate was calculated in cc/minute. By this method, the $HSiCl_3$ flowrate could be kept constant for long periods of time with high accuracy, for example 1.00 $\pm$0.02 cc/minute. By a combination of nitrogen pressure and capilliary tubing size, flowrates of $HSiCl_3$ from 0.25 to 5.0 cc/minute could be readily provided. The liquid $HSiCl_3$ coming out of the capilliary tubing was vaporized in a preheater and then fed into the A-21 resin bed reactor.

A series of experiments on the disproportionation of $HSiCl_3$ was carried out at 60° and at atmospheric pressure. Results were summarized in Table II. Data in Table II showed that the rate of disproportionation of $HSiCl_3$ was much slower than that of H_2SiCl_2 under the same experimental conditions. For example, over 50% of H_2SiCl_2 were reacted in 1.8 seconds residence time in the A-21 resin bed in comparison with only 5% $HSiCl_3$ disproportionation in the same residence time. In 3.6 seconds, the H_2SiCl_2 disproportionation reached equilibrium to yield 14% SiH_4 which was the equilibrium concentration of

TABLE II

RELATIVE RATE OF DISPROPORTIONATION OF H_2SiCl_2 AND $HSiCl_3$ OVER 10 GRAMS OF A-21 RESIN CATALYST AT 60°, ATMOSPHERIC PRESSURE

Experiment Number	Chlorosilane	Feedrate[1] (cc/Minute)	Residence Time[2] (Second)	Product Composition, Mole %				
				SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	$SiCl_4$
1	H_2SiCl_2	564	1.8	10.52	14.09	43.67	31.66	0.07
2	$HSiCl_3$	460	2.0	--	0.03	2.20	95.59	2.18
3	$HSiCl_3$	549	1.8	--	0.02	2.14	95.45	2.34
4	$HSiCl_3$	277	3.7	--	0.04	2.92	93.39	3.65
5	$HSiCl_3$	137	7.4	--	0.12	4.69	89.91	5.28
6	H_2SiCl_2	564	1.8	10.45	13.51	43.05	32.91	0.08
7	H_2SiCl_2	282	3.6	14.07	11.93	36.31	37.54	0.15

[1]cc/Minute of vapor at 60°.

[2]Base on void space in A-21 resin bed.

SiH_4 observed previously. In the case of $HSiCl_3$ disproportionation, the yield of H_2SiCl_2 was about 3% which was far from the equilibrium concentration of about 10% H_2SiCl_2. Extrapolation of the rate data on the disproportionation of $HSiCl_3$ in Table II gave approximately 15 to 20 seconds residence time which might be required to reach equilibrium concentration of 10% H_2SiCl_2. Thus, the rate of disproportionation of $HSiCl_3$ in the vapor phase was faster than that of the same disproportionation reaction of $HSiCl_3$ in the liquid phase which required about 1 to 2 minutes to reach equilibrium. However, the throughput in a liquid phase disproportionation would be much higher than that of a vapor phase disproportionation through a given A-21 resin bed, since the liquid density was about 200 times the vapor density. In conclusion, there appeared to be no advantages to perform the disproportionation of trichlorosilane in the vapor phase. The rate data on the disproportionation gave the following order of reactivity,

$$H_3SiCl > H_2SiCl_2 > HSiCl_3$$

C. Purification of SiH_4

The only major impurity in SiH_4 prepared by the disproportionation reaction would be chlorosilanes such as H_3SiCl. Although most chlorosilanes in the product mixture would be removed by physical means such as distillation and condensation by cold trap or low temperature scrubbing, the trace amount of remaining chlorosilanes could be conveniently removed by adsorption with activated carbon as proposed by W. C. Breneman. Sistersville has selected the commercial Pittsburgh Activated Carbon Type OL for the mini-plant to make solar grade SiH_4. The following experiments were carried out to test this material for the purification of SiH_4.

The apparatus for the purification of SiH_4 was schematically shown in Figure 2 attached. As shown in Figure 2 the crude SiH_4 coming from the disproportionation of H_2SiCl_2 through a dry-ice cold trap at -78° could be directed by the 3-way stopcock either to the in-line gas chromatograph or to the activated carbon column (1.5 cm x 15 cm weighed 10 grams). The purified SiH_4 coming out of the activated column could be readily analyzed by the in-line gas chromatograph. The crude SiH_4 was produced at a constant rate of 64 cc/minute by minute by feeding 500 cc/minute of H_2SiCl_2 into 10 g of A-21 resin at 81°.

The SiH_4 crude coming out of a dry-ice cold trap at -78° was analyzed several times during the course of the experiment to give an average composition of:

	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$
Mole, %	97.9	1.88	0.22	0.03
Weight, %	95.4	3.80	0.67	0.12

The crude SiH_4 contained 4.59% by weight of chlorosilanes which is probably too much from a process point of view. However, the crude SiH_4 was well-suited for experimental purposes. The crude SiH_4 was fed into the activated carbon column. The composition of the crude SiH_4 and the purified SiH_4 were analyzed by the in-line gas chromatograph during the course of the experiment. Results were summarized in Table III. Data in Table III showed that the activated carbon effectively removed the chlorosilanes in the crude SiH_4 to a level beyond the limit of detection of the gas chromatograph instrument. The limit of detection was about 5 ppm. A plot of residual chlorosilanes in the purified SiH_4 versus weight percent of chlorosilanes adsorbed on the

FIGURE 1 APPARATUS FOR PURIFICATION OF SiH_4

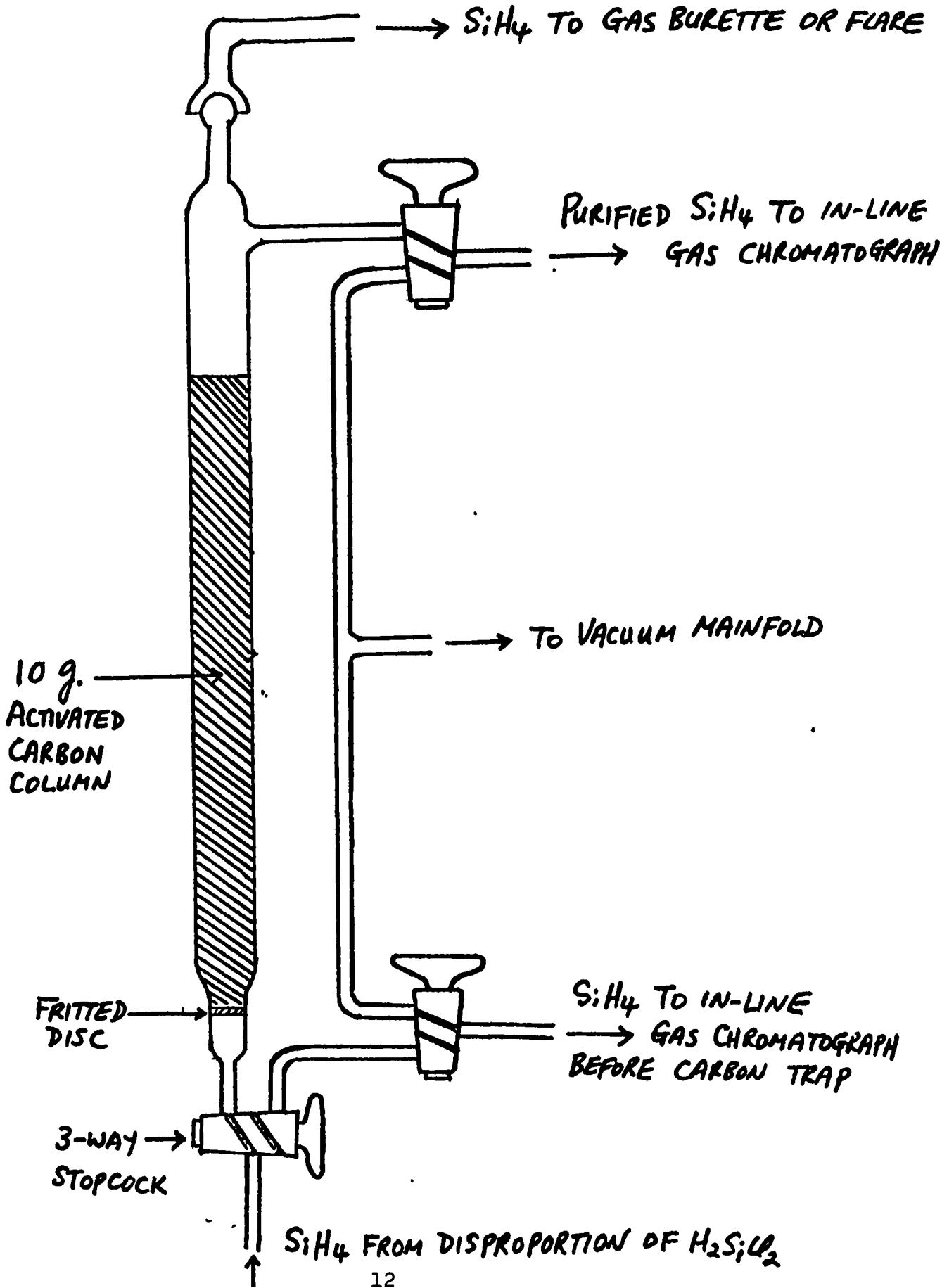

TABLE III

PURIFICATION OF SiH_4 BY ACTIVATED CARBON

(BASED ON 10 GRAMS OF PITTSBURGH ACTIVATED CARBON TYPE OL)

Time (Hr)	Total Volume of SiH_4 Fed (Liters)	SiH Feed In Mole (Gram)	Composition of Purified SiH_4 In Mole Percent				Total Amount Adsorbed Chlorosilanes (Gram)
			SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	
0.5	1.92	0.079 (2.54)	100	ND*	ND	ND	0.12
1.0	3.84	0.159 (5.26)	100	ND	ND	ND	0.23
1.5	5.76	0.238 (7.84)	100	ND	ND	ND	0.36
2.5	9.60	0.397 (13.1)	100	ND	ND	ND	0.60
3.5	13.4	0.554 (18.2)	100	ND	ND	ND	0.84
4.5	17.3	0.714 (23.5)	100	ND	ND	ND	1.08
4.75	18.2	0.752 (24.8)	99.98	0.015	ND	ND	1.14
5.08	19.5	0.806 (26.5)	99.92	0.085	ND	ND	1.22
5.33	20.5	0.846 (27.9)	99.79	0.21	ND	ND	1.28
5.67	21.8	0.901 (29.7)	99.52	0.48	ND	ND	1.36
6.33	24.3	1.00 (32.9)	98.92	1.04	0.052	ND	1.51
6.58.	25.3	1.04 (34.4)	98.78	1.12	0.11	ND	1.58

* ND = Not Detected, limited of detection was about 5 ppm.

activated carbon was shown in Figure 3. The data points for ND were arbitrarily plotted at 2.5 ppm in order to show continuity of the graph. As shown in Figure 3, a sharp rise of residual chlorosilane occurred at about 11% by weight of chlorosilane adsorbed on the activated carbon. In other words, 100 g of activated carbon type OL could effectively remove about 11 g of chlorosilanes from the impure SiH_4 while maintaining the residual chlorosilanes in the purified SiH_4 at a low level of, say, less than 10 ppm. It was noted that when SiH_4 was passed into the activated carbon bed, the carbon column immediately became hot. A close examination of this phenomenon showed that the source of heat appeared to be generated from the reaction of SiH_4 with impurities adsorbed on the activated carbon, e.g., water and oxygen. When a fresh sample of 10 g activated carbon Type OL was dried at 200° in a stream of 75 cc/minute of dry nitrogen for 1 hour, water was liberated from the carbon (about 0.3 g H_2O). The heat-treated activated carbon did not generate significant amount of heat in contrast to the untreated material when SiH_4 crude was fed into purification column. The experiment was continued and the purity of SiH_4 coming out of the purifier was analyzed. Results were summarized in Table IV. Data in Table IV showed that the heat-treated activated carbon effectively removed chlorosilane impurities as previously reported. These data readily defined the effectiveness as well as limitation of this activated carbon for the purification of SiH_4.

Attempts were made to regenerate the spent carbon column by heating. An electric heater was placed around the carbon column. It was heated to a selected temperature while dry nitrogen gas passed through at about 75 cc/minute. Three temperatures, 150°, 250°, and 350° were selected for the experiment. The treated carbon column was cooled to room temperature and tested with the

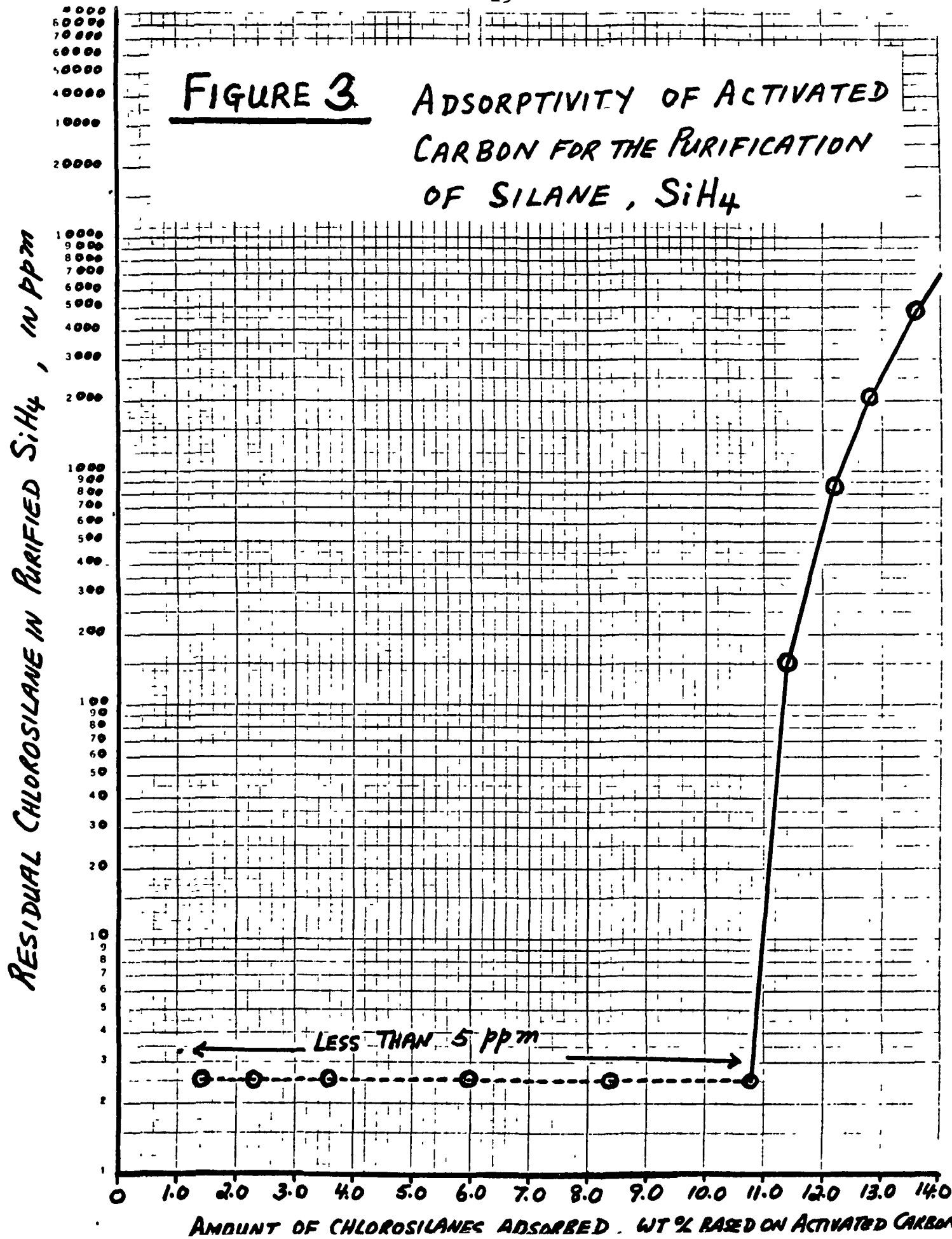
FIGURE 3
ADSORPTIVITY OF ACTIVATED CARBON FOR THE PURIFICATION OF SILANE, SiH4
RESIDUAL CHLOROSILANE IN PURIFIED SiH4, IN PPM
LESS THAN 5 ppm
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
AMOUNT OF CHLOROSILANES ADSORBED. WT % BASED ON ACTIVATED CARBON

TABLE IV

PURIFICATION OF SiH_4 BY ACTIVATED CARBON

(Based on 10 Grams of Pittsburgh Activated Carbon Type OL)

Time (Hour)	Total Volume of SiH_4 Fed (Liters)	SiH_4 Feed Mole In (Gram)	Composition of Purified SiH_4 In Mole %				Total Amount Adsorbed Chlorosilanes (Gram)
			SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	
0.5	1.92	0.079(2.54)	100	ND*	ND	ND	0.12
1.5	5.76	0.238(7.84)	100	ND	ND	ND	0.36
2.5	9.60	0.397(13.1)	100	ND	ND	ND	0.60
3.0	11.5	0.476(15.7)	100	ND	ND	ND	0.72
3.5	13.4	0.554(18.2)	100	ND	ND	ND	0.84
4.0	15.3	0.633(20.8)	100	ND	ND	ND	0.96
4.5	17.3	0.714(23.5)	100	ND	ND	ND	1.08
5.0	19.2	0.794(26.2)	99.995	0.005	ND	ND	1.20
5.5	21.1	0.873(28.8)	99.75	0.25	ND	ND	1.32
6.0	23.0	0.952(31.4)	99.67	0.33	ND	ND	1.44

* ND = Not Detected, limit of detection was about 5 ppm.

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same SiH_4 crude. Results were summarized in Table V. Data in Table V showed that the spent activated carbon could not be regenerated to its original activity. As shown in Table V, heat treatment at 150° and 250° was not effective at all. At 350° for 1 hour, the heat-treated carbon column showed less than half of its original adsorbility. It appeared that some of the chlorosilanes were irreversibly adsorbed on the carbon surface. In conclusion, activated carbon was an effective adsorbent to remove chlorosilane impurities from SiH_4. The activated carbon should be tested for adsorbed impurities prior to use. As in the present study, substantial amount of water and heat were generated when SiH_4 crude was passed into an untreated activated carbon column. This could be a serious problem in large scale operations.

D. Hydrogenation of $SiCl_4$ and The Direct Synthesis of H_2SiCl_2

The hydrogenation of $SiCl_4$ to $HSiCl_3$ was briefly studied and reported previously.[1] Temperature profile measurement along the Cu/Si mass bed in this reaction,

$$3\ SiCl_4 + Si + 2\ H_2 \xrightarrow{Cu} 4\ HSiCl_3 \qquad (2)$$

showed a mild exotherm at the top of the fluidized bed reactor ($\Delta T \sim 10°$).

In order to understand the reaction mechanism, it was necessary to study the quality of fluidization and the heat transfer characteristic of the one-inch laboratory fluidized bed reactor used in these experiments. The well-known HCl + Si reaction was chosen as a model reaction. It is a facile reaction and is strongly exothermic, which was well-suited for this purpose.

TABLE V

REGENERATION OF SPENT ACTIVATED CARBON BY HEATING

(Based on 10 Grams of Pittsburgh Activated Carbon Type OL)

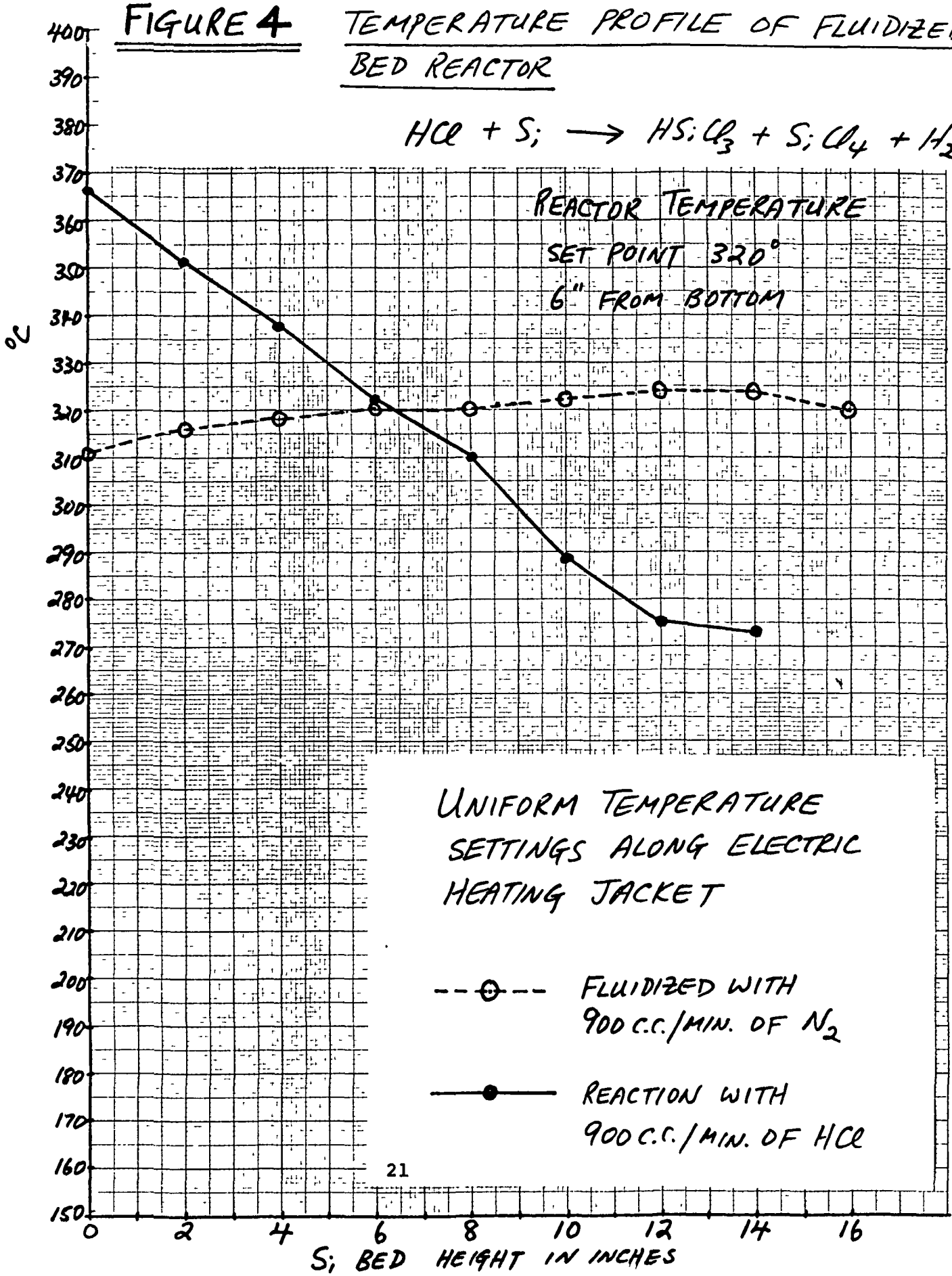
Time (Hour)	Total Volume of SiH_4 Fed (Liter)	SiH_4 Feed In Mole (Gram)	Composition of Purified SiH_4 In Mole %				Total Amount Adsorbed Chlorosilanes (Gram)
			SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$	
(Heat-Treated at 150° for 30 Minutes)							
1.0	3.84	0.159(5.26)	99.83	0.17	ND	ND	0.23
1.5	5.76	0.238(7.84)	99.80	0.20	ND	ND	0.36
(Heat-Treated at 250° for 30 Minute)							
0.25	0.96	0.040(1.31)	99.995	0.005	ND	ND	0.058
1.0	3.84	0.159(5.26)	99.99	0.01	ND	ND	0.23
2.0	7.68	0.318(10.5)	99.94	0.055	ND	ND	0.46
2.5	9.60	0.397(13.1)	99.89	0.11	ND	ND	0.60
(Heat-Treated at 350° for 1 Hour)							
0.75	2.88	0.119(3.95)	100	ND	ND	ND	0.173
1.5	5.76	0.238(7.84)	100	ND	ND	ND	0.36
2.25	8.64	0.358(11.8)	99.995	0.005	ND	ND	0.518
2.75	10.6	0.437(14.5)	99.91	0.087	ND	ND	0.633
3.25	12.5	0.517(17.1)	99.74	0.26	ND	ND	0.748

The HCl + Si reaction was carried out at 320° with 900 cc/minute of HCl feed. Temperature in the Si mass bed was measured by thermocouples located at various heights of the bed. The first experiment was carried out with equal settings on the electric heaters in the heating jacket to provide uniform heating and cooling along the fluidized bed reactor. After 30 minutes of reaction, temperatures along the Si mass bed were measured and plotted against the bed height as shown in Figure 4. The graph in Figure 4 showed that during the HCl + Si reaction, the bottom of the Si bed was much hotter than that at the top with a temperature spread of about 100°. This temperature profile could be readily explained by the facile, strongly exothermic HCl + Si reaction which occurred mostly at the bottom of the fluidized bed.

In order to compensate for the large temperature deviations in the HCl + Si reaction, the electric heaters in the heating jacket were reset to give a lot more heating at the top and very little at the bottom of the reactor. The temperature profile of the heating jacket was shown by the dotted line --⊡--- in Figure 5. At these settings, the top of the mass bed was at about 400° while it was less than 100° at the bottom. Then, the Si metal was fluidized with 900 cc/minute of nitrogen gas, which corresponded to zero heat of reaction. The temperature profile of the Si mass bed while fluidized with nitrogen was shown by the dotted --○--- line in Figure 5. Interestingly, fairly uniform temperatures along the Si mass bed resulted despite a 300° temperature spread along the heating jacket. Thus, the mixing of Si mass in the reactor was suprisingly good in such a small diameter fluidized bed. Next, the nitrogen gas was replaced with 900 cc/minute of HCl. The temperature profile along the mass bed during the HCl + Si reaction was shown by the solid ——●—— line in Figure 5. As shown in Figure 5, uniform temperature along the Si mass bed as achieved.

FIGURE 4 TEMPERATURE PROFILE OF FLUIDIZED BED REACTOR

$$HCl + Si \longrightarrow HSiCl_3 + SiCl_4 + H_2$$



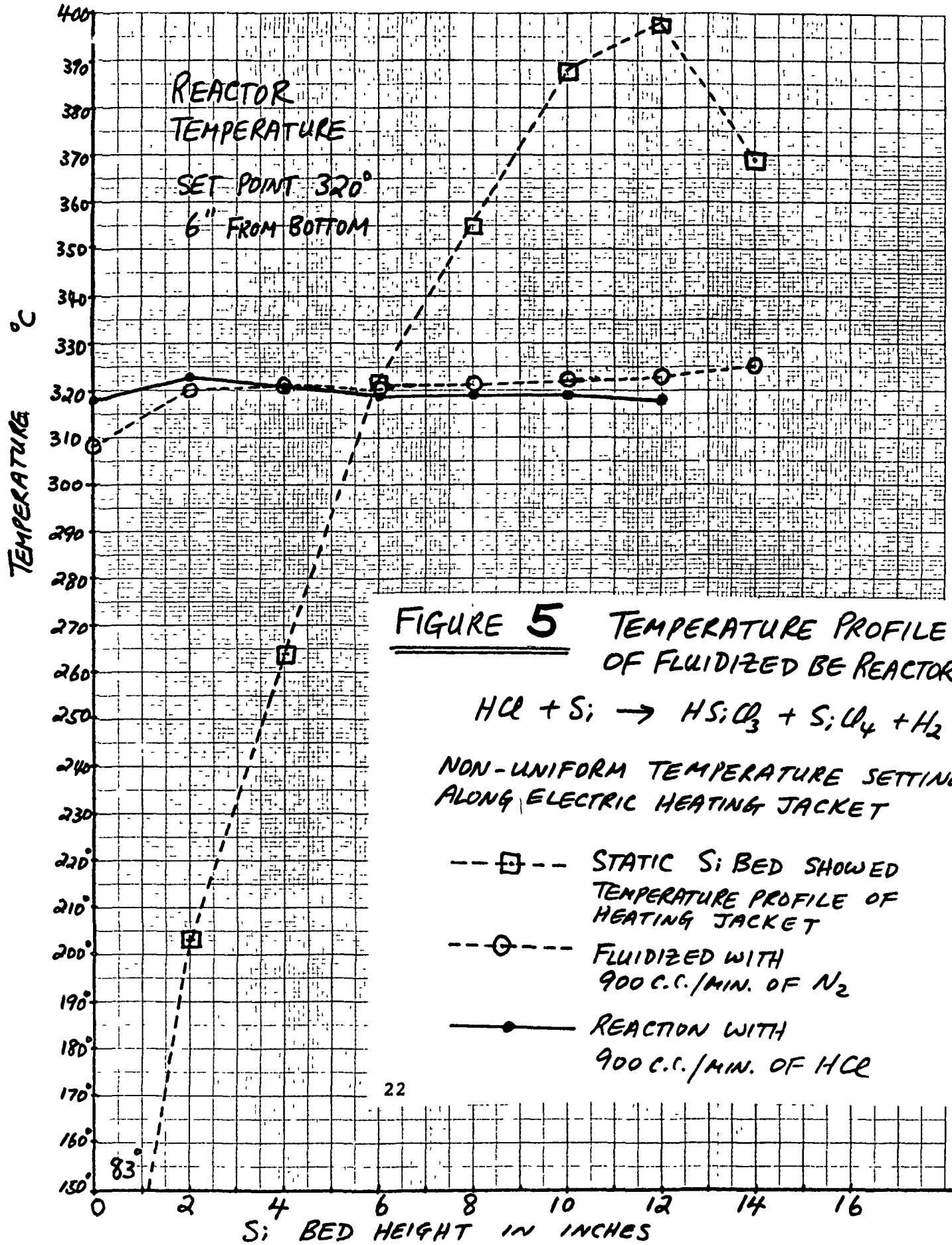


FIGURE 5 TEMPERATURE PROFILE OF FLUIDIZED BE REACTOR

$HCl + Si \rightarrow HSiCl_3 + SiCl_4 + H_2$

NON-UNIFORM TEMPERATURE SETTINGS ALONG ELECTRIC HEATING JACKET

- STATIC Si BED SHOWED TEMPERATURE PROFILE OF HEATING JACKET
- FLUIDIZED WITH 900 C.C./MIN. OF N_2
- REACTION WITH 900 C.C./MIN. OF HCl

The hydrogenation of $SiCl_4$ to $HSiCl_3$ over a Cu/Si mass might be looked at as two reaction steps,

(a) a slow hydrogenation step,

$$3\ SiCl_4 + 3\ H_2 \xrightarrow{Cu} 3\ HSiCl_3 + 3\ HCl \qquad (3)$$

followed by a facile reaction

(b) $$3\ HCl + Si \xrightarrow{Cu} HSiCl_3 + H_2 \qquad (4)$$

A simple thermodynamic calculation by Dr. J. M. Berty of Union Carbide gave $\Delta\ H_2° = +3.19$ k cal/g mole $HSiCl_3$ for reaction (3) and $\Delta\ H_2° = -51.2$ k cal/g mole $HSiCl_3$ for reaction (4). The overall reaction (3) + (4) showed a slightly exothermic reaction with $\Delta\ H° = -10.4$ k cal/g mole $HSiCl_3$. Thus, the temperature profile of the Cu/Si mass bed in the hydrogenation of $SiCl_4$ to $HSiCl_3$ might be explained by a slow, slightly endothermic hydrogenation reaction (3) at the lower part of the reactor followed by a facile, strongly exothermic reaction (4) near the top of the mass bed.

Since copper was used as catalyst in these reactions, it would be interesting to compare the HCl + Si reaction in the presence of copper with the same reaction in the absence of copper. The Si + HCl reaction was repeated at 280°. At this temperature, only 23% of the 900 cc/minute of HCl were reacted with no copper present. On the other hand, the same reaction with a Cu/Si mass containing 1% copper catalyst at 280° gave 100% reaction. Thus, copper catalyzed the HCl + Si reaction as generally believed. An interesting observation was made on

the direct synthesis of H_2SiCl_2 from the above experiments. When a fresh Cu/Si mass was reacted with HCl gas at 320°, the trichlorosilane crude was analyzed for dichlorosilane. Results of these analyses were summarized in Table VI.

What is interesting about the data in Table VI is the high yield of H_2SiCl_2 during the first few percent of the HCl + Si reaction. The yield of dichlorosilane was about 11% at the first instant of the reaction. The H_2SiCl_2 yield dropped off rapidly. In less than 30 minutes of reaction, the H_2SiCl_2 yield was back to the level 1.5% to 2% as previously reported.

E. Miscellaneous Data Collected

1. Stability of H_3SiCl on Storage

A sample of H_3SiCl was prepared by cryogenic distillation and stored in a stainless steel cylinder for calibration purposes. After two months of storage at room temperature, this sample of monochlorosilane was again analyzed. As the following data showed, about 10% of the H_3SiCl were disproportionation to SiH_4, H_2SiCl_2 and $HSiCl_3$ after two months

Component	SiH_4	H_3SiCl	H_2SiCl_2	$HSiCl_3$
Freshly Prepared	0.46	97.13	2.21	0
After Two Months	5.36	78.92	6.50	0.05

2. Calibration of In-line Gas Chromatograph

An electronic integrator, Model 3380A manufactured by Hewlett Packard, Palo Alto, California, was purchased and installed. Previous analysis of gas chromatographic data was performed by planimetry which was a time-consuming process. The electronic integrator much simplified the procedure for data collecting

TABLE VI

INITIAL REACTIONS OF HCl WITH Cu/Si CONTACT MASS AT 320°

Analysis Number	HCl Feed (cc/Minute)	$HSiCl_3$ Crude (Gram)	Si Reacted* (%)	Composition of $HSiCl_3$ Crude, Mole %		
				H_2SiCl_2	$HSiCl_3$	$SiCl_4$
1	900	6.0	0.6	10.9	86.3	1.7
2	900	12.0	1.8	7.5	88.6	2.0
3	900	10.0	2.8	5.2	90.6	2.3
4	900	50.5	7.9	1.4	91.5	5.2

* Based on 200 grams Cu/Si charge.

and saved a great deal of manual labor. The instrument was calibrated with a standard mixture of SiH_4, H_3SiCl, H_2SiCl_2, $HSiCl_3$ and $SiCl_4$ in approximately the same molar ratio as obtained in the disproportionation experiments. A known standard of 13.95% mole SiH_4, 13.28% mole H_3SiCl, 40.95% mole H_2SiCl_2, 29.24% mole $HSiCl_3$ and 2.58% mole $SiCl_4$ was analyzed by the in-line gas chromatograph and the peak area calculation by the electronic integrator gave 7.80% SiH_4, 9.67% H_3SiCl, 43.64% H_2SiCl_2, 35.59% $HSiCl_3$ and 3.30% $SiCl_4$. The Response Factor (or Sensitivity Factor, mole/unit area) were calculated to give: SiH_4 = 1.79, H_3SiCl = 1.37, H_2SiCl_2 = 0.938, $HSiCl_3$ = 0.822 and $SiCl_4$ = 0.782. The previously determined Response Factors by planimetry were: SiH_4 = 1.89, H_3SiCl = 1.33, H_2SiCl_2 = 0.938, $HSiCl_3$ = 0.840 and $SiCl_4$ = 0.584. Thus, the two methods of Response Factor determination were in good agreement with the exception of $SiCl_4$. Because of the small amount of $SiCl_4$ in the standard sample, the peak area measurement for $SiCl_4$ by planimetry was done at a higher (16X) sensitivity scale than all the other chlorosilanes and SiH_4. The non-linearity of the attenuation of scale sensitivity accounted for the large difference in the Response Factor for $SiCl_4$.

II. Pilot Plant Studies

A. Mini-plant Construction

The process piping for the dichlorosilane to silane mini-plant is 95% complete. At this writing the only lines remaining are the dichlorosilane feed, the product silane gas lines to the exterior of the building, and the safety valve vent lines. The circulating refrigeration system is complete

and has been leak tested. The instrument panel was completed and moved into place. The process connections have been made. All of the instruments have been calibrated and aligned including the process flowmeters, temperature and pressure sensors, and the precision micrometer needle valves used on the chromatograph sampling system.

A pre-start up safety review team has been formed with representation from the Sistersville Plant Engineering, Production, Safety and Research Department. The task of this Team, as is required in any Union Carbide facility, is to review the installation and process to assure that appropriate safety standards are being met and that especially in cases of unique processing that the facility will operate in a safe manner. The initial briefing for the Team was held and included a detailed description of the process, a flow chart review and site inspection.

Photographs showing the progress of construction are presentation in Figure 6 through 9. The instrument panel shown in Figure 6 has been laid out to allow for the additional instruments required for the later inclusion of the maxi-plant. The "erector set" style steel framework is expandable also. The sampling system panel shown in Figure 7 will connect the individual sampling points on the process units to the chromatograph which is within four feet of the area of the photograph. The selector valves will choose which stream to feed to the chromatograph, the others would then bypass to a vent. The precision metering valves are used to control the sample flowrate. In Figure 8 the condenser details are shown. The silane still and its associated condenser system is in the foreground. The vapors from the top of the still flow down through the shell and tube condenser. This will allow sub-cooling of the vapor and increased purity of the non-condensable SiH_4. In the disengaging pot, the liquid dichlorosilane/monochlorosilane mixture is separated from

FIGURE 6

SILANE MINI-PLANT

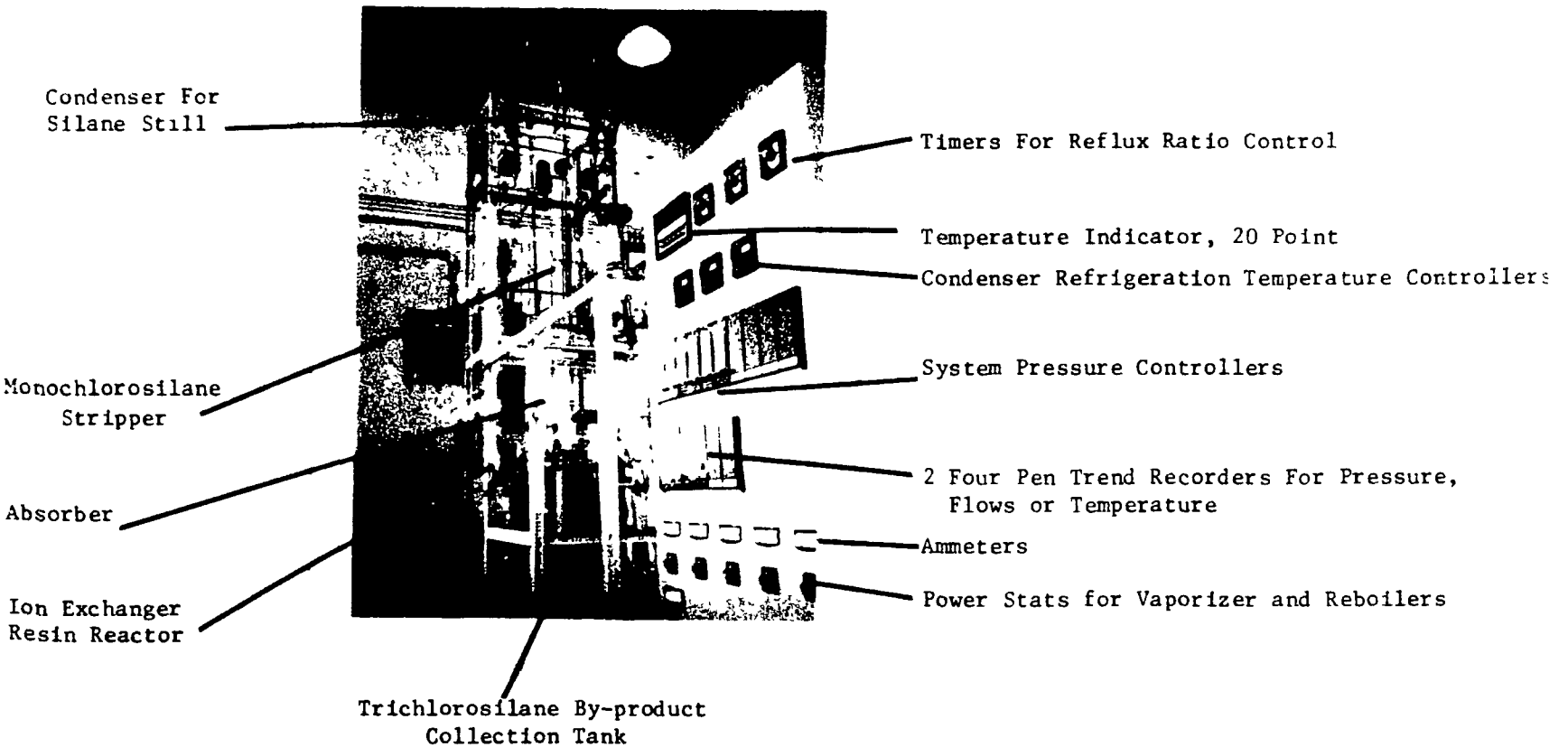
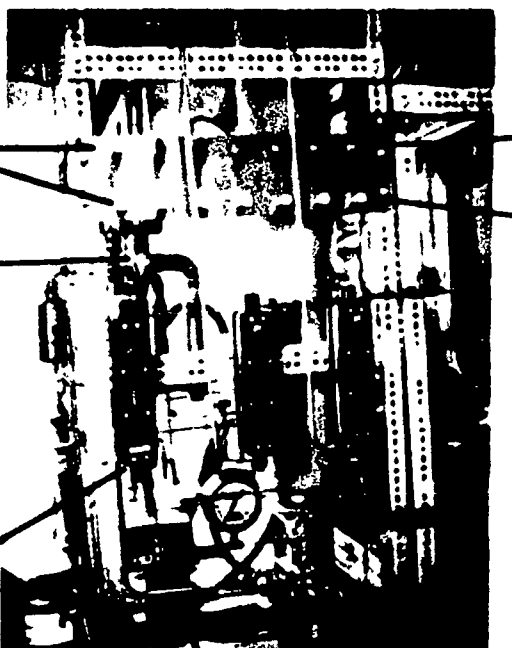

Condenser For Silane Still
Timers For Reflux Ratio Control
Temperature Indicator, 20 Point
Condenser Refrigeration Temperature Controllers
System Pressure Controllers
Monochlorosilane Stripper
2 Four Pen Trend Recorders For Pressure, Flows or Temperature
Absorber
Ammeters
Ion Exchanger Resin Reactor
Power Stats for Vaporizer and Reboilers
Trichlorosilane By-product Collection Tank

FIGURE 7

SILANE MINI-PLANT

SAMPLE STREAM SELECTION PANEL


Helium Carrier Control Valves
Silane Still Reboiler Section
Flowmeters for Indicating Rate of Internal Recycle (H_3SiCl, $SiCl_4$, H_2SiCl_2)
Three-Way Sample Selection Valve
Sample Flow Control Valve
Orifice and Differential Pressure Meter For Feed to Reaction

the vapor SiH_4. Reflux to the column is controlled by an electrical timer which alternately supplies 110 VAC power to the windings of two solenoid valves. Since one valve is normally open, and the other normally closed, a flow switching is accomplished to provide either reflux or make. The monochlorosilane-silicon tetrachloride stripper in the background of Figure 8 is identical to the silane still configuration. The other feature illustrated in Figure 8 is the safety relief set up. Each major equipment arrangement which could be isolated from the rest of the process is equipped with a safety relief device. This consists of a rupture disc assembly, a telltale gauge, and a spring loaded relief valve all in series. The rupture disc is set at the maximum allowable working pressure of the system (150 psi in this case). The disc serves to assure a leak-free system and proper operation of the relief valve. The gauge is used to verify the integrity of the disc. (No pressure should be present if the disc is intact.) The relief valve, also set at 150 psi, is used to allow controlled relief and prevent suck-back of air after relieving.

In Figure 9, the heart of the circulating refrigeration unit is shown. The refrigerant, R-11, is circulated by the pump through coils immersed in a cold bath and then to the individual condensers. The condenser temperatures are controlled by electrically operated valves which allow the refrigerant to flow through or bypass the condenser. The expansion tank allows the system to sustain thermal cycling. The cold bath will consist of a mixture of R-113 (trichlorotrifluoroethane) and ethanol chilled by dry-ice. This bath is not flammable at room temperature, does not freeze at -78°C and has a boiling point of above ambient.

FIGURE 8

SILANE MINI-PLANT

CONDENSER DETAIL

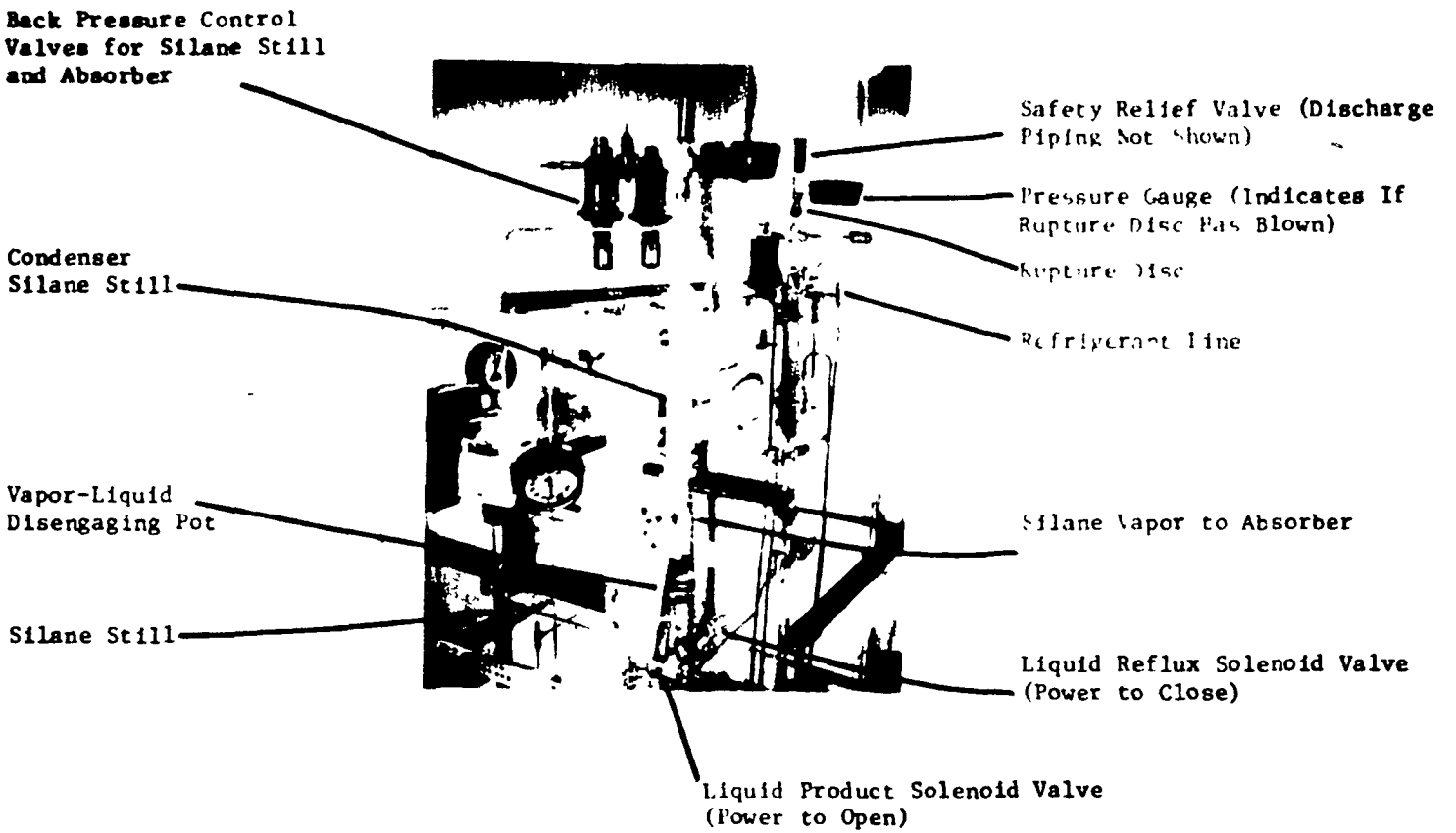
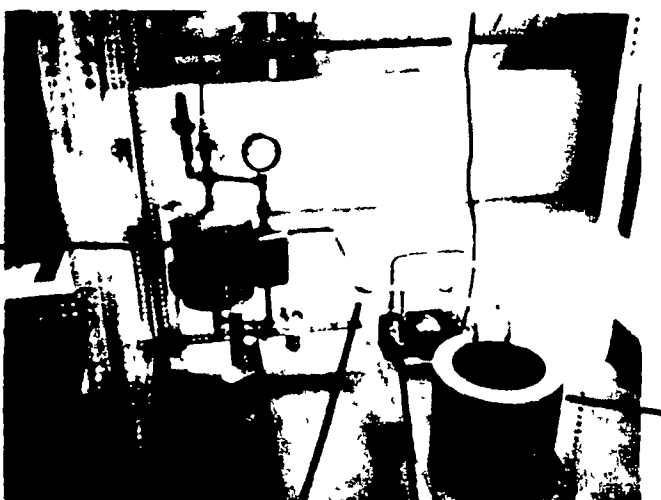

Back Pressure Control Valves for Silane Still and Absorber
Safety Relief Valve (Discharge Piping Not Shown)
Pressure Gauge (Indicates If Rupture Disc Has Blown)
Rupture Disc
Refrigerant Line
Condenser Silane Still
Vapor-Liquid Disengaging Pot
Silane Vapor to Absorber
Silane Still
Liquid Reflux Solenoid Valve (Power to Close)
Liquid Product Solenoid Valve (Power to Open)

FIGURE 9

REFRIGERATION DETAIL

SILANE MINI-PLANT



B. Storage of Silane

On the storage of silane, the feasibility of using carbon as an adsorbent to lower storage pressure/increase volumetric efficiency was investigated. An apparatus as shown in Figure 10 was assembled. Two stainless steel, 150 cc capacity vessels, one completely filled with 62.4 g of dried carbon were connected in parallel to a source of silane. A graduated inverted burette immersed in silicone oil was connected to the system to measure the volume of SiH_4 which would be evolved from either cylinder. The carbon was Pittsburgh Type OL, an acid washed anthracite coal based carbon of high porosity. (Table VII) The carbon was dried at 200°C and 0.5 mm of mercury for 24 hours. The silane was electronic grade from Linde Specialty Gas. After thoroughly evacuating the system with a pump for 24 hours, silane from the source was allowed to pressurize both cylinders to 100 psi. The cylinder containing carbon warmed up from 22° to 29°C. The system was allowed to reach thermal equilibrium of 22°C. Then the individual cylinders were vented via the gas burette and the displaced volume and cylinder pressure recorded. During the desorption, the carbon filled cylinder did cool off slightly. The desorption was done slowly to allow approach to thermal equilibrium. Figure 11 shows that at constant pressure significantly more SiH_4 can be stored and released from a given volume when that volume is filled with activated carbon then when it is not At 100 psi, nearly three times the amount of silane is available over the normal storage method. Also, the work required to compress and store a given quantity of silane is reduced by a factor of three or more. At 100 psig storage pressure, the "packing density" of silane was 0.0143 g/cc as the free gas versus 0.0359 g/cc adsorbed on carbon. Samples of the silane adsorbed on carbon will be analyzed to determine if a change in trace impurities has occurred. It should be noted that other types of carbon which may be more effective were not tested, however, a Japanese patent reference claimed 40 cc SiH_4/g of carbon where as we obtained 70 cc SiH_4/g at the same pressure (142 psia).[2]

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FIGURE 10

BY DATE SUBJECT SHEET NO. OF
CHKD BY DATE Silane Adsorption Apparatus JOB NO

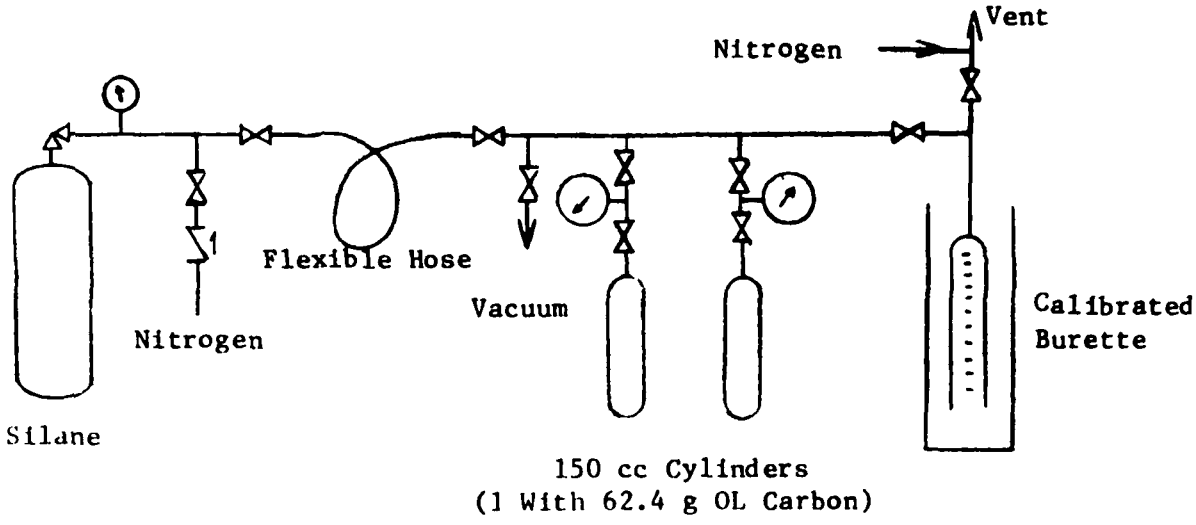

FIGURE 11

Adsorption of Silane on Carbon

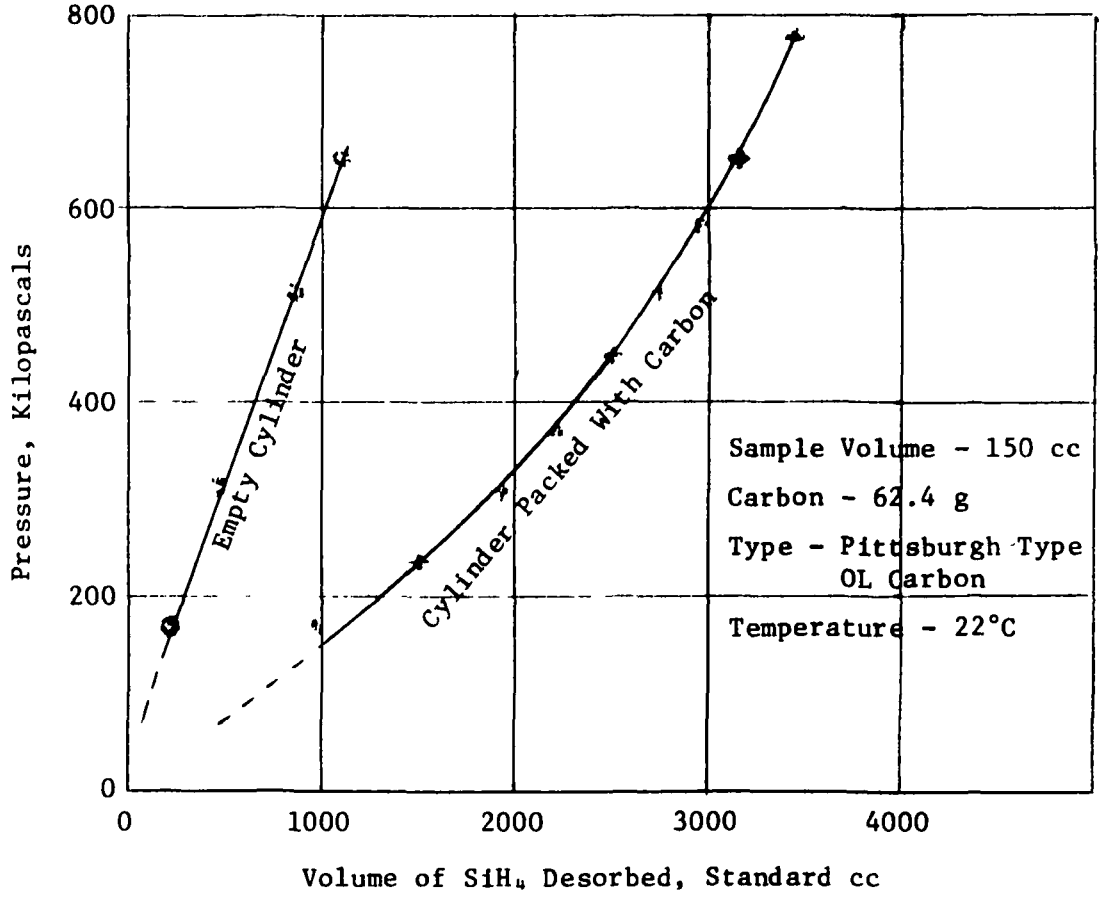

TABLE VII

PROPERTIES OF PITTSBURGH ACTIVATED CARBON TYPE OL

Total Surface Area (N_2, BET Method), m^2/g	1000
Apparent Density, g/cc	0.45
Particle Density (Hg Displacement), g/cc	0.75
Real Density (He Displacement), g/cc	2.2
Pore Volume, cc/g	0.88
Voids In Dense Packed Column, %	40
Specific Heat at 100°C	0.25
Mesh Size, U. S. Sieve Series	20 x 50
Iodine Number	<1000
Ash, %	<8
Moisture (Typical Commercial Material), %	2

C. Design Calculations

1. Silane/Dichlorosilane Still

The redistribution reactor effluent may be assumed to be composed of equilibrium mixture of silanes. Based on the data of J. Y. P. Mui, one composition could be:

	Mole %
SiH_4	8.25
H_3SiCl	9.95
H_2SiCl_2	37.90
$HSiCl_3$	43.70
$SiCl_4$	0.2

The separation of this stream into a vapor fraction rich in SiH_4, a liquid fraction rich in H_2SiCl_2 with substantially no $HSiCl_3$ and a second liquid fraction rich in $HSiCl_3$ and with substantially no H_2SiCl_2 is the duty of the silane/dichlorosilane still. To accomplish this separation it is planned to use a continuous still which employs a partial condenser whose coolant temperature is controlled to allow the SiH_4 rich vapor to escape uncondensed. In order to reduce the refrigerant load (SiH_4 boils at approximately -112°C at 1 atmosphere) the unit will be operated under pressure. As a preliminary model, 60 psia was chosen. At this pressure, H_2SiCl_2 boils at 58°C.

To calculate the theoretical plate and reflux ratio requirements, the recovery of H_2SiCl_2 and $HSiCl_3$ must be specified (other specifications in lieu of these are possible, of course). The value used in the initial design was a 90% recovery of H_2SiCl_2 in the distillate, 95% recovery of $HSiCl_3$ in the distilland. Assuming constnat relative volatility of the components and using the Gilliland correlation, a column of 12.6

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stages operating at 1.55 reflux ratio would achieve the separation. The assumption of constant relative volatility is not completely accurate but for a preliminary evaluation it is adequate. The product stream compositions would be expected to be:

	Mole %	
	Distillate	Distilland
SiH_4	15.14	0
H_3SiCl	18.26	0
H_2SiCl_2	62.59	8.33
$HSiCl_3$	4.01	91.23
$SiCl_4$	0	0.44

The bubble point and dew point of the distillate at 60 psia were calculated to be -32°C and +43°C respectively. To achieve a recovery of SiH_4 by using a partial condenser to condense primarily H_2SiCl_2, a 44% recovery of SiH_4 at a purity of 67.6 mole percent could be achieved at -5°C equilibrium temperature. Higher recovery but at correspondingly lower purity could be achieved at higher equilibrium condenser temperatures. Thus the overall column could separate the reactor effluent into the following streams (Table VIII).

The distillation unit designed for the silane mini-plant is 1-inch diameter by 54-inches high and is packed with steel gauze packing with a height equivalent to a theoretical stage of 2 to 2.5 inches or approximately 22 theoretical stages.

TABLE VIII

SILANE/DICHLOROSILANE STILL COMPOSITIONS

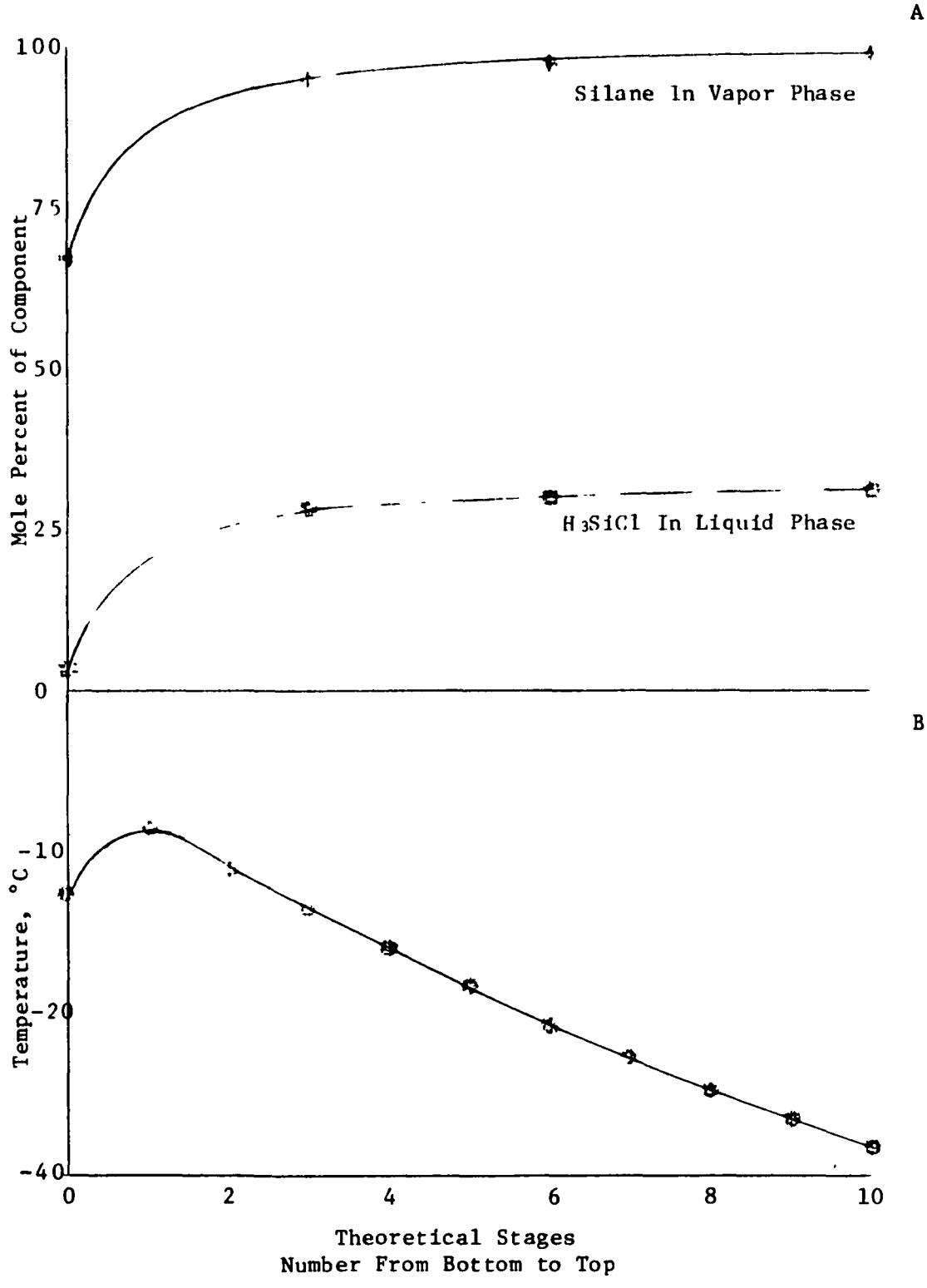
	Mole %			
		Distillate		
	Feed	Liquid	Vapor	Distilland
SiH_4	8.25	9.39	0.676	0
H_3SiCl	9.95	18.42	0.168	0
H_2SiCl_2	37.9	67.79	0.151	8.33
$HSiCl_3$	43.7	4.39	0.040	91.23
$SiCl_4$	0.2	0	0	0.44
Total Mass	100	40.72	2.69	56.7

2. Absorber

The effluent vapor from the silane/dichlorosilane still will be fed to an absorber which uses cold silicon tetrachloride to absorb the mono- and dichlorosilanes. A calculation was made using the method of Edmister to determine the expected absorber efficiency under a set of proposed operating conditions. The design goal was to achieve a purity of silane gas of at least 99 mole percent, using as a raw gas feed a material whose composition was the same as the vapor distillate in Table VIII. The chlorosilanes would be absorbed using cold (-40°C) silicon tetrachloride which contained 2.5 mole percent H_3SiCl. The vapor and liquid fugacities were assumed to be ideal and the component enthalpies as determined from Watson's correlation. The result of this exercise was that an absorber which used one mole of liquid $SiCl_4$ per 5 moles of raw gas could achieve a silane purity of 99.1% in 10 theoretical stages. The liquid, entering at -40°C would be expected to exit at -5°C. A plot of the anticipated temperature and composition profile is shown in Figure 12. The column specified in the design of the mini-plant is 4-foot high by 1-inch I.D., packed with 1/4-inch Ceramic Intalox saddles, this column should be more than adequate for the task.

D. Gas Chromatograph Calibration

The Hewlett Packard Model 5830A reporting chromatograph was calibrated and programmed for analysis of the hydrochlorosilane products and intermediates. This instrument will be used for on-line sampling and analysis of the various streams in the silane mini-plant. The chromatograph was fitted with a 12-inch long x 1/8-inch diameter column packed with 20% dimethylsilicone on Chromasorb WDMC. A gas sampling valve with a 0.5 cc sample

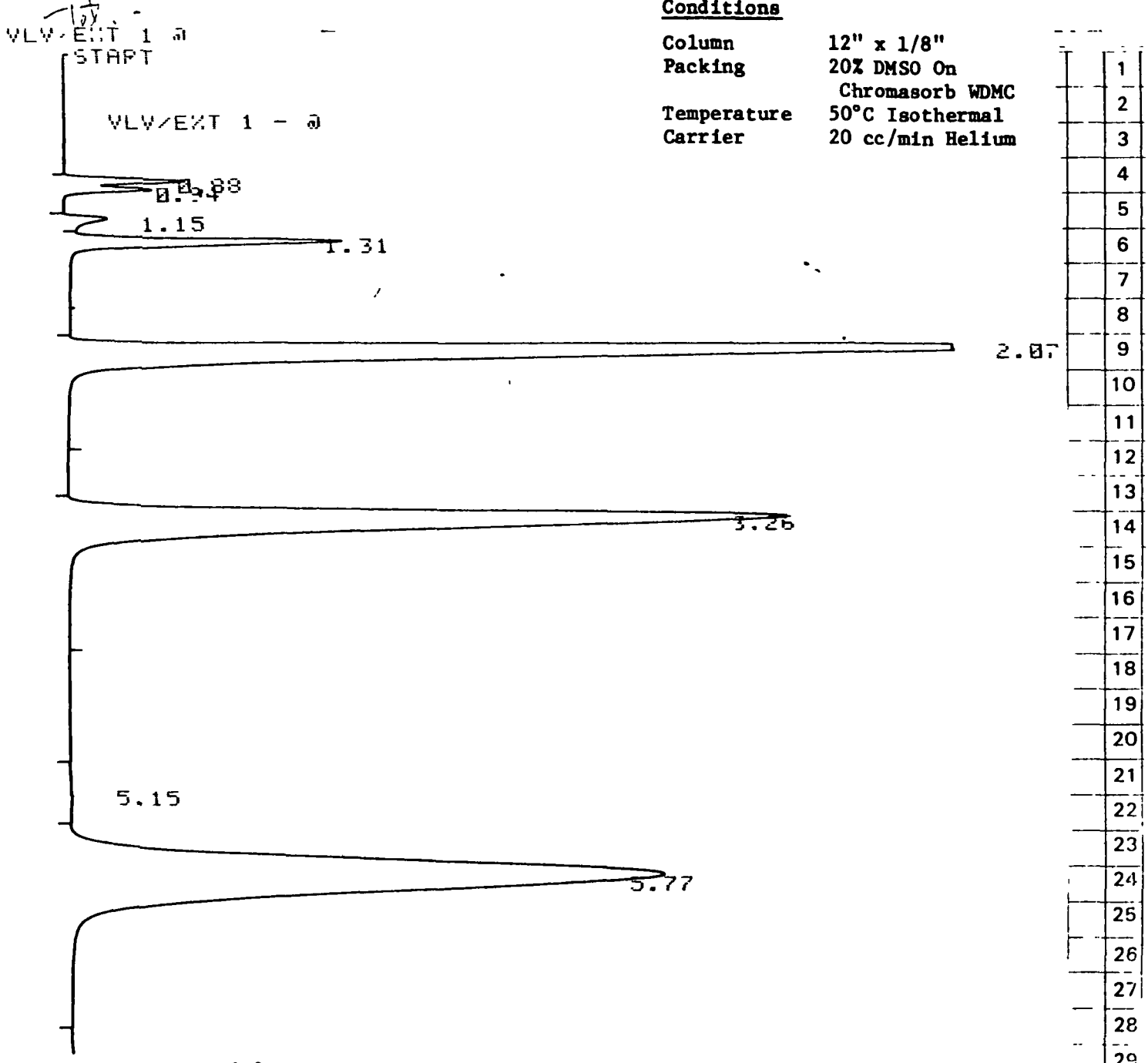

A
100
75
50
25
0
Mole Percent of Component
Silane In Vapor Phase
H3SiCl In Liquid Phase
B
-10
-20
-40
Temperature, °C
0
2
4
6
8
10
Theoretical Stages
Number From Bottom to Top

loop was also installed to allow accurate, reproducible sample volumes to be injected. The column was conditioned by repeated injection of a mixture of chlorosilanes over a one week period. This served to condition the column, check-out system operation and allow verification of optimal oven temperatures and elution times to be made. A scan of a typical mixture of the five silanes $H_xSiCl_{4-x}(0 < x < 4)$ is shown in Figure 13. This sample also contains a small amount of N_2 and HCl which orginate from the H_2SiCl_2.

To determine detector sensitivity, pure compounds were injected using the gas sample injection valve and the relative area counts obtained. The silane was obtained from Linde Specialty Gas and had a purity of > 99%. The monochlorosilane was obtained from a sample distilled by J. Y. P. Mui and was 88.5% pure. The dichlorosilane was obtained from typical commercial material at this site and was 97.2% pure. The silane, monochlorosilane or dichlorosilane were each injected as a gas at atmospheric pressure via the gas sample valve. Since the sample size was constant, equal number of moles of each component was used and thus the area count was a direct measure of detector sensitivity. A purity correction for each component was made by dividing the area count of the pure component by the area percent. Since the least pure sample, H_3SiCl was still 88.5%, the maximum error introduced here would be less than 12% even if the sensitivities of the other materials were vastly different from H_3SiCl. The relative response factors for SiH_4, H_3SiCl and H_2SiCl_2 were found by dividing the areas by the area for H_2SiCl_2. Actually the inverse or moles per area is required in the chromatograph's computer so those values were then inverted. The values are:

FIGURE 13

SUBJECT chromatographic standard ; dichlor, trichlor, silicon



Conditions

Column	12" x 1/8"
Packing	20% DMSO On Chromasorb WDMC
Temperature	50°C Isothermal
Carrier	20 cc/min Helium

hp 5830A Ref. 2068-8
AREA %

RT	AREA	AREA %	
0.88	11770	1.318	N_2
0.94	8126	0.910	SH_4
1.15	6351	0.711	HCl ?
1.31	39230	4.393	H_2S, Cl
2.07	245190	27.445	H_2S, Cl_2
3.26	240400	26.919	$HSCl_3$
5.15	6775	0.870	
5.77	341400	38.228	$SiCl_4$

	Moles/Area/Area of H_2SiCl_2
SiH_4	1.467
H_3SiCl	1.258
H_2SiCl_2	1.000

The factors for $HSiCl_3$ and $SiCl_4$ were determined by preparing a weighed mixture of liquid H_2SiCl_2, $HSiCl_3$ and $SiCl_4$ all of which were individually 98+% pure. The liquid mixture was injected (5 μ liters) and the area response measured. The relative response factors were then determined to be:

H_2SiCl_2	1.000
$HSiCl_3$	0.7454
$SiCl_4$	0.5078

A plot of response factor versus Cl atoms is shown in Figure 14.

E. Economic Analysis of Silane Process

A block diagram and material balance for a silicon-to-silane facility with recycle of $SiCl_4$ is shown in Figure 15. The basis for the recycle streams is for 100% efficiency in the redistribution reactions, 2% loss of hydrogen per pass through the hydrogenation unit, 90% silicon efficiency and essentially complete separation of trichlorosilane from $SiCl_4$ in the dichlorosilane reactor section. The subsequent Figures 16 through 18 show a breakdown of the process blocks and the additional recycle process streams. Computer modeling of the various stills is in progress to determine process energy requirements.

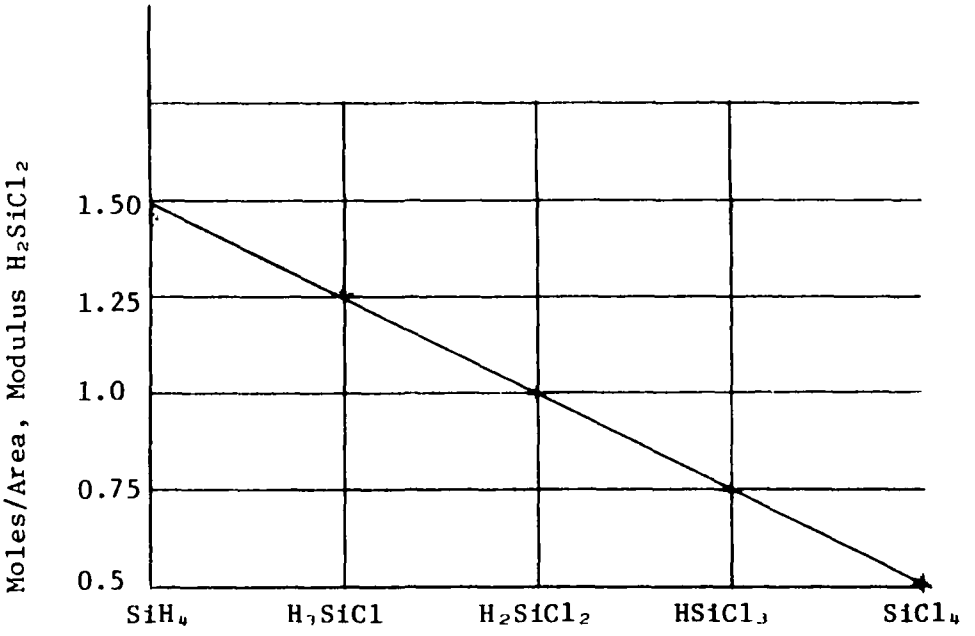
UNION CARBIDE CORPORATION FIGURE 14

SISTERSVILLE PLANT

BY DATE SUBJECT Gas Chromatograph Sensitivity Factors For Hydro-chlorosilanes SHEET NO OF

CHKD BY DATE JOB NO

HP Model	5830A
Column	12" x 1/8"
Packing	20% Dimethylsilicone on Chromasorb WDMC
Temperature	Isothermal 50°C



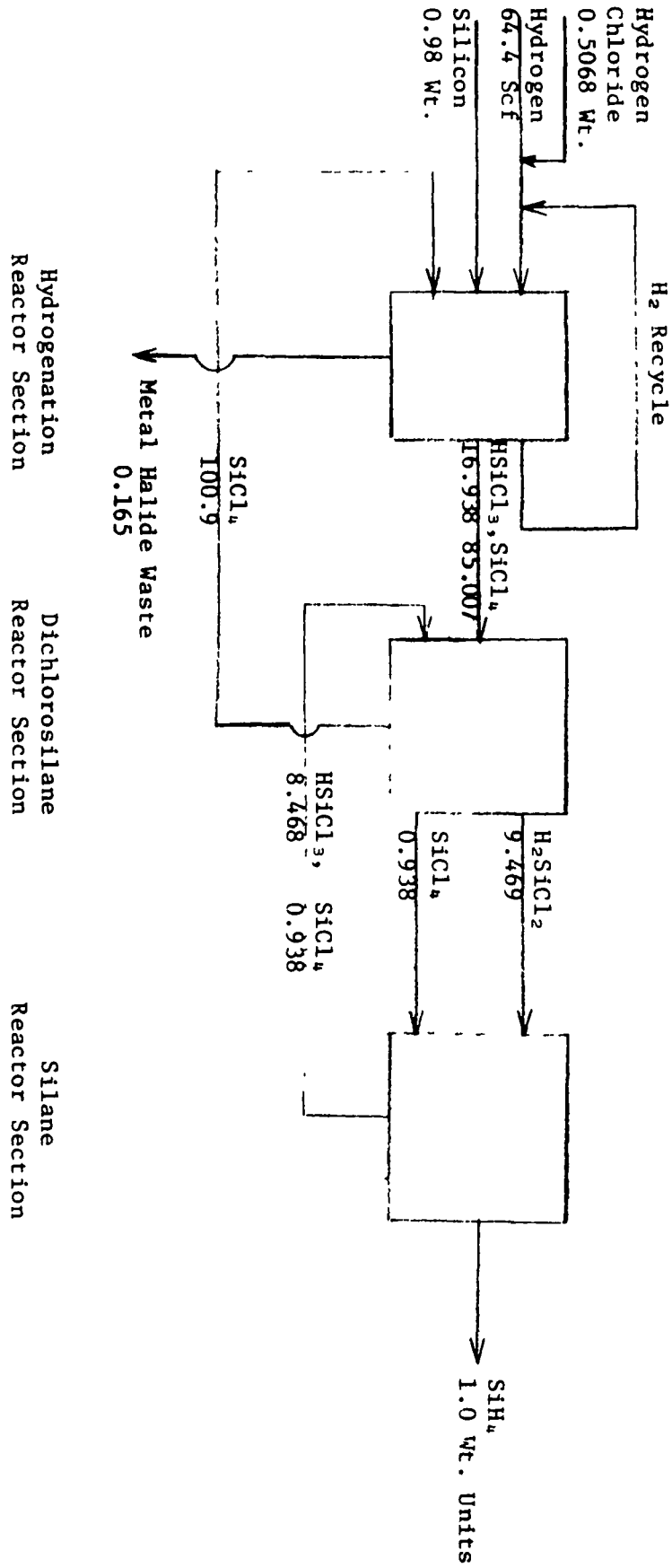
UNION CARBIDE CORPORATION

SISTERSVILLE PLANT

FIGURE 15

BY WCB DATE 7-15-76 SUBJECT Silane From Silicon Block Diagram SHEET NO OF

CHKD BY DATE JOB NO



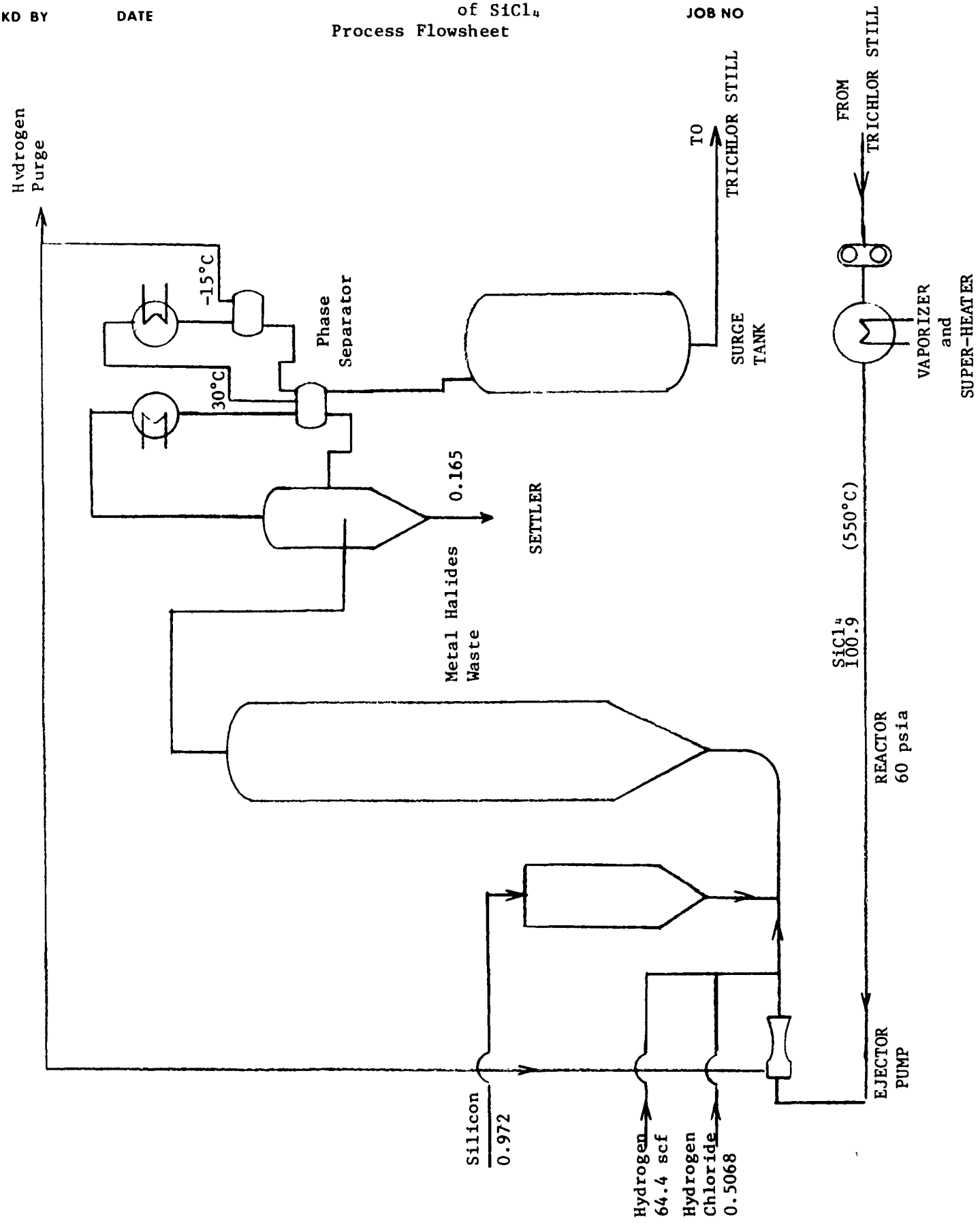
UNION CARBIDE CORPORATION FIGURE 16

SISTERSVILLE PLANT

BY WCB DATE 7-15-76 SUBJECT Trichlorosilane Via Hydrogenation of $SiCl_4$ SHEET NO OF

CHKD BY DATE JOB NO

Process Flowsheet

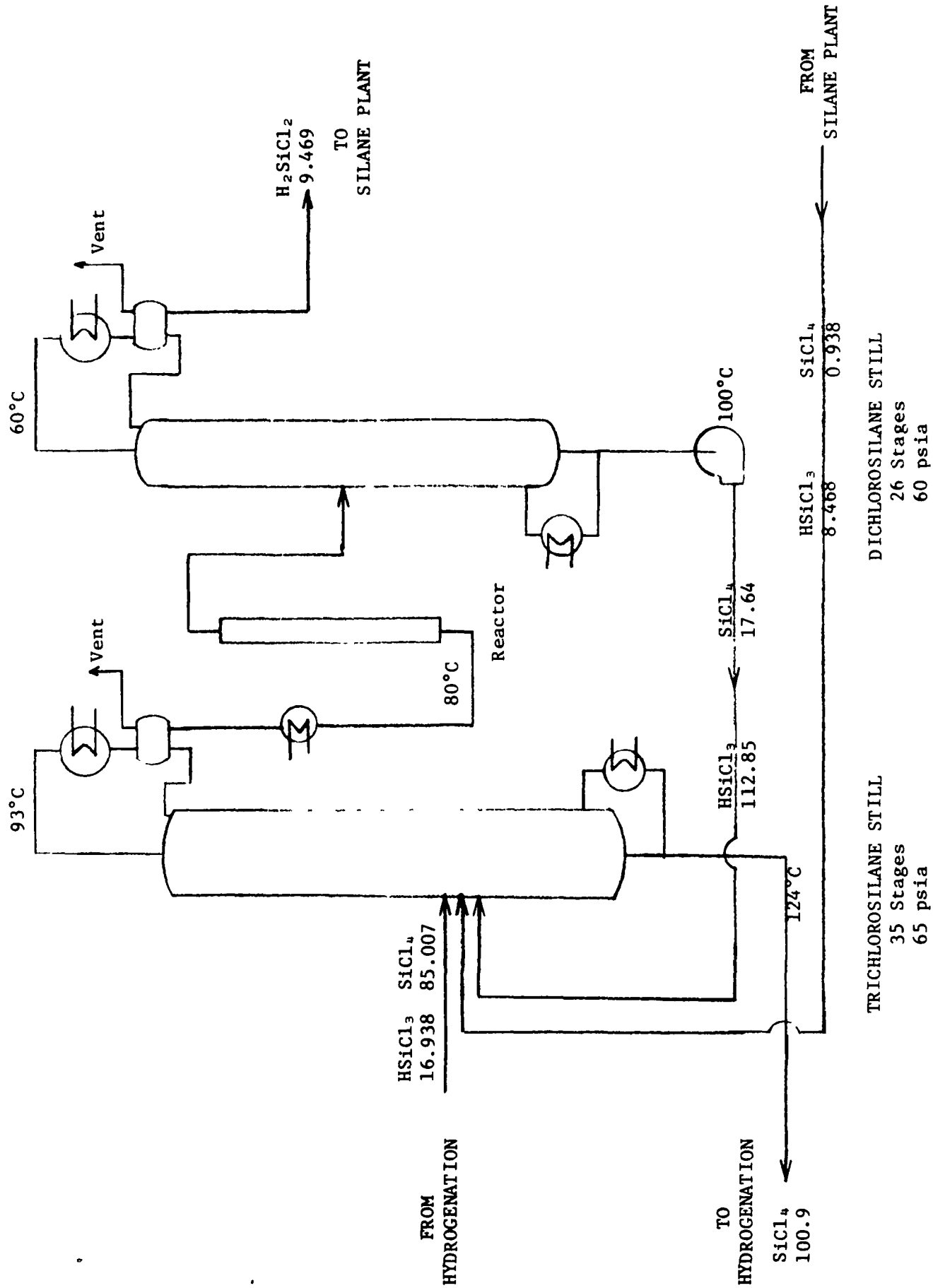


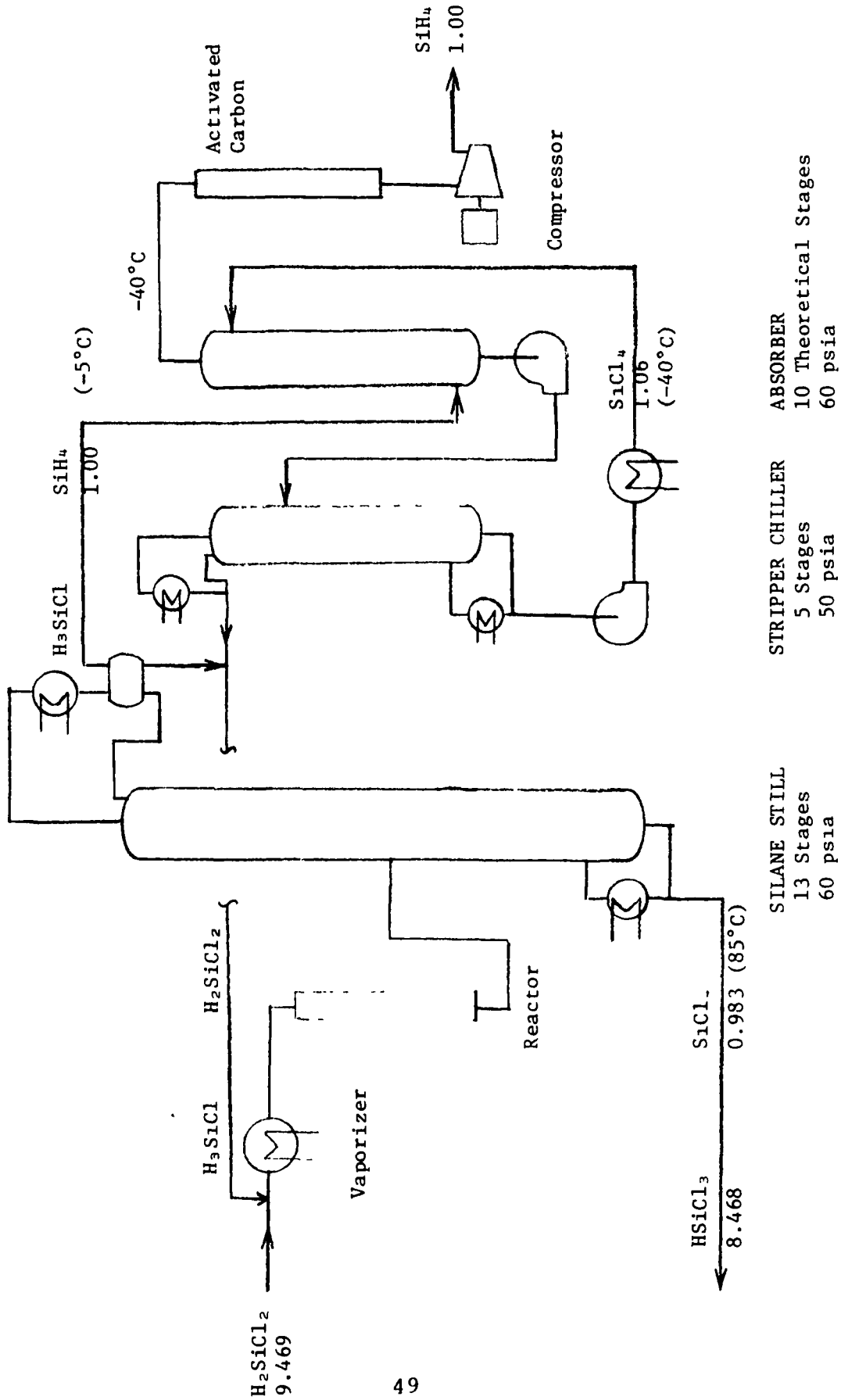
UNION CARBIDE CORPORATION FIGURE 17

SISTERSVILLE PLANT

BY WCB DATE 7-15-76 SUBJECT Dichlorosialne From Trichlorosilane Process Flowsheet SHEET NO OF

CHKD BY DATE JOB NO




SiH4
1.00
Activated Carbon
Compressor
-40°C
(-5°C)
SiH4
1.00
SiCl4
1.06
(-40°C)
H3SiCl
H2SiCl2
H3SiCl
Vaporizer
Reactor
SiCl4
0.983 (85°C)
HSiCl3
8.468
H2SiCl2
9.469
STRIPPER CHILLER
5 Stages
50 psia
ABSORBER
10 Theoretical Stages
60 psia
SILANE STILL
13 Stages
60 psia

CONCLUSIONS

The kinetics of the vapor phase redistribution of trichlorosilane indicate that there is no advantage to vapor phase versus liquid phase contact. Although the vapor phase reaction rate is higher than the liquid phase rate, the difference does not overcome the difference in reactant density. The liquid phase reaction system has a higher mass throughput capability.

The storage of silane as either an in-plant buffer or for packaging in containers suitable for inter-state shipment can possibly be improved through the use of activated carbon in the storage containers. Increased volumetric efficiency and increased safety at lower storage pressure is possible by completely filling the storage container with granulated activated carbon and absorption of silane on the carbon.

The mini-plant for producing up to 10 lb/day of SiH_4 is nearing construction completion. This unit should demonstrate the economic and product quality potential of the chlorosilane redistribution process.

PROJECTED FIFTH QUARTER ACTIVITIES

- The silane from dichlorosilane mini-plant will be brought on-stream to produce ten pounds SiH_4 per day.
- The preliminary planning and design of a maxi-plant to prepare SiH_4 from $HSiCl_3$ will be completed.
- Additional fundamental studies on the redistribution reaction mechanism will be carried out.
- Pending contractual agreement, a reactor to study the hydrogenation of $SiCl_4$ to $HSiCl_3$ will be designed and constructed

PROGRAM STATUS UPDATE

Updated versions of the approved program plan and labor and cost summaries are shown in Figures 19, 20 and 21. The "initial operation" of the mini-plant is about nine week behind schedule due mainly to delays in delivery of major equipment items.

NEW TECHNOLOGY

No new technology is presented in this report which has been developed under the scope of Contract 954334.

BIBLIOGRAPHY

1. Breneman, W. C., Mui, J. Y. P., LSSA Project Quarterly Report, June 23, 1976.

2. Asauo, M., Oohashi, T., Shimazak, Ye, Japanese Patent 74 54, 298, May 27, 1974.

Figure 19
Implementation Plan

▲ Decision Milepost

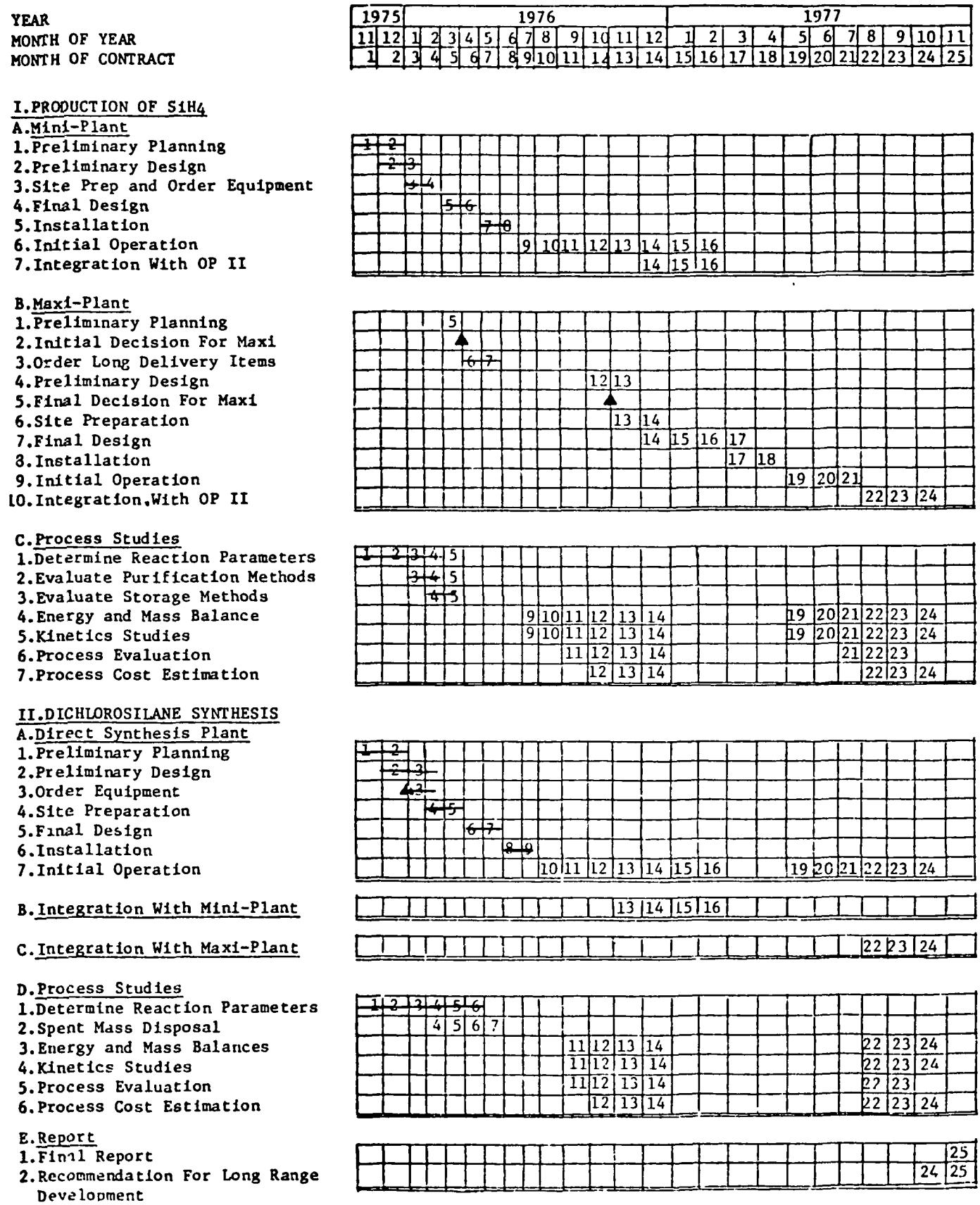


FIGURE 20

UNION CARBIDE CORPORATION

SISTERSVILLE PLANT

BY WCB DATE 12/1/75 SUBJECT Direct Labor Hours Planned For High Volume, Low Cost Silane Project (Revised) SHEET NO OF

CHKD BY DATE JOB NO 954334

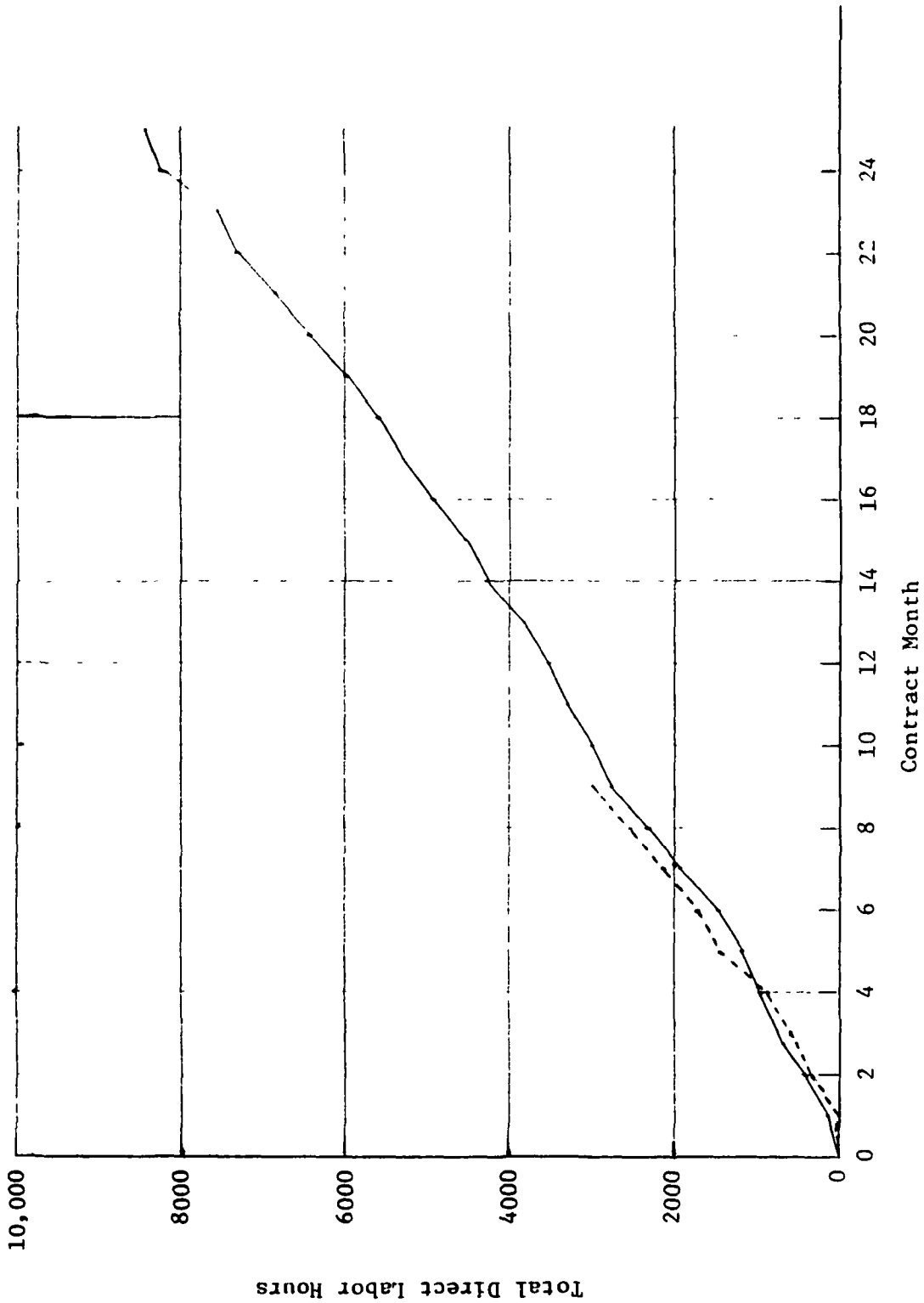


FIGURE 21

UNION CARBIDE CORPORATION

SISTERSVILLE PLANT

BY WCB DATE 12/1/75 SUBJECT Total Cost Plan For Low Cost Silane Project (Revised) SHEET NO. OF

CHKD BY DATE JOB NO. 954334